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Magma storage conditions of large Plinian eruptions of Santorini Volcano (Greece)

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ABSTRACT

The intensive variables in dacitic-rhyodacitic magmas prior to four large Plinian eruptions of Santorini Volcano over the last 200 ka (Minoan, Cape Riva, Lower Pumice 2 and Lower Pumice 1) were determined by combining crystallization experiments with study of the natural products, including the volatile contents of melt inclusions trapped in phenocrysts. Phase equilibria of the silicic magmas were determined at pressures of 1, 2 and 4 kbar, temperatures of 850-900°C, fluid (H₂O+CO₂)-saturation, XH₂O [= molar H₂O/(H₂O+CO₂)] between 0.6 and 1 (melt H₂O contents of 2 - 10 wt%), and redox conditions of FMQ or NNO+1. Experiments were generally successful in reproducing the phenocryst assemblage of the natural products. The phase relationships vary significantly among the investigated compositions, revealing a sensitivity to small variations in whole rock compositions. Our results show that pre-eruptive storage conditions of the four silicic magmas were all very similar. The magmas were stored at T = 850 – 900°C and P ≥ 2 kbar, under moderately reduced conditions (ΔNNO = - 0.9 to - 0.1), with melts poor in fluorine (~500-800 ppm) and sulphur (≤ 100 ppm), but rich in water and chlorine (5-6 wt%, ca. 2500-3500 ppm, respectively). In all cases, melts were slightly undersaturated with respect to H₂O, but most probably saturated with respect to H₂O+Cl ± CO₂ and a brine. The Santorini magma plumbing system appears to be dominated by a large, long-lived (≥ 200 ka) predominantly-silicic magma storage region situated at ≥ 8 km depth, from which crystal-poor melt batches were extracted during the largest caldera-forming eruptions of the volcanic system.

KEY WORDS

Magma storage; Melt inclusions; Phase equilibrium; Santorini; Volatiles
INTRODUCTION

It has been increasingly recognized that dramatic changes in magma storage conditions can occur over very short periods of time at a single volcano. This was shown at, for example, Mt. St Helens and Mt. Vesuvius, where magma storage depths vary over timescales of several hundreds of years (e.g., between the Pompeii and Pollena eruptions at Mt. Vesuvius; Scaillet et al., 2008) to a few years (between the Wn and We events at Mt. St Helens; Gardner et al., 1995; Blundy et al., 2008; Rutherford & Devine, 2008). These variations of magma ponding level may be attributed to differences in the volatile content and buoyancy of ascending magmas. They might also be related to changes in stress imposed on the crustal plumbing system by the overlying edifice (e.g., Pinel & Jaupart, 2003; Pinel et al., 2010), following either caldera formation (Ventura et al., 1999) or volcano spreading (Borgia et al., 2005). It is remarkable indeed that, for these two volcanic systems, the largest and fastest pressure drops recorded by the magmas coincide with the partial destruction of the edifice subsequent to a major explosive eruption. Strain relaxation in the upper crust resulting from a decrease of edifice load could allow accumulation of magmas at shallower depths (Ventura et al., 1999). Variations of magma storage conditions have also been correlated with changes in eruptive dynamics at Mt. Pelée, Mt. Vesuvius and Tenerife (e.g., Martel et al., 1998; Scaillet et al., 2008; Andújar & Scaillet, 2012a; Andújar & Scaillet, 2012b). For instance, Andújar & Scaillet (2012b) showed that the explosive-effusive style of phonolitic magmas correlates with the amount of volatiles, the degree of water-undersaturation and the depth of magma storage, the explosive character generally increasing with pressure, depth and dissolved water content. Determining magma storage conditions over time is thus crucial to understanding volcano behaviour, and may significantly contribute to the evaluation of volcanic hazards during periods of unrest.
Santorini volcano (South Aegean Arc, Greece), which has recently shown signs of seismic and geodetic unrest (2011-2012; e.g., Newman et al., 2012), is an ideal target for unraveling these potential relationships, as its history is marked by recurrent large-scale Plinian eruptions (ca. every 20-30 ka). Some of these eruptions triggered caldera collapses, alternating with edifice construction and minor interplinian eruptions (Fig. 1). This study focuses on the silicic products of the four major Plinian eruptions of Santorini that have occurred over the last 200 ka (Fig. 1): the Lower Pumice 1, Lower Pumice 2, Cape Riva and Minoan eruptions. Magmas of Lower Pumice 1, Lower Pumice 2 and Minoan were dominantly rhyodacitic, and that of Cape Riva was dacitic. In order to define precisely the P, T, fO$_2$ and volatile (H$_2$O, CO$_2$, Cl, F, S) pre-eruptive storage conditions of these magmas, we carried out phase equilibrium crystallization experiments coupled with a petrological and geochemical study of the natural products. We present the stability fields of the phases for each eruption over the T-P-fO$_2$-XH$_2$O conditions explored: T = 850-900°C, P = 1, 2 and 4 kbar, fO$_2$ = FMQ and NNO+1, and XH$_2$O [= moles of H$_2$O/ (H$_2$O+CO$_2$)] between 1 (i.e., H$_2$O-saturated) and 0.6 (H$_2$O-undersaturated). The phase assemblages, abundances and compositions of the experimental and natural products are compared, and their implications for pre-eruptive conditions and for our understanding of the Santorini plumbing system are discussed.

**GEOLOGICAL BACKGROUND**

**Eruptive history**

Volcanism at Santorini began ca. 650 ka and subsequently involved two major explosive cycles between ~360 and ~3.6 ka that formed the bulk of the volcanic deposits (Druitt et al., 1999). Twelve major Plinian eruptions occurred during the two cycles, with ejected volumes ranging from a few km$^3$ to several tens of km$^3$. The first explosive cycle
(360-172 ka) included five major Plinian eruptions, while the second cycle (172-3.6 ka) included seven (Fig. 1). The average time interval between these main eruptions was about 20 to 30 ka. Interplinian activity between the main explosive eruptions involved extrusive edifice construction and minor (subplinian or less) explosive activity (Huijsmans & Barton, 1986; Druitt et al., 1999; Vespa et al., 2006). All Santorini magmas belong to the calc-alkaline series, and range compositionally from basalt to rhyodacite; no rhyolite has been documented onland at Santorini except in the oldest (Akrotiri) sequences. Deposits of the major Plinian eruptions are compositionally zoned, but can be subdivided into those that are dominantly andesitic and those that are dominantly silicic (Druitt et al., 1999). The dominantly silicic eruptions occur at the end of each cycle (Fig. 1).

The second cycle terminated with the Bronze-Age Minoan eruption (3.6 ka). Since then, effusive activity has constructed a ~3 km$^3$ dacitic lava shield on the floor of the Minoan caldera (Kameni Islands, 197 BC to AD 1950; Pyle & Elliott, 2006; Fig. 1). Since 1950, and until recently, activity on the Kameni islands has been characterized by the emission of low-temperature (< 100°C) fumarolic gases. However, between January 2011 and March 2012, increases of seismic activity, water temperature and CO$_2$ levels (e.g., ISMOSAV website; Papazachos et al., 2012), were accompanied by inflation of the northern part of the caldera (Newman et al., 2012; Parks et al., 2012). This has been attributed to the intrusion of 10–20 million m$^3$ of magma at about 4.4 km depth during this period (Parks et al., 2012).

**The four dominantly-silicic Plinian eruptions studied in this paper**

The Lower Pumice 1 (LP1) and Lower Pumice 2 (LP2) eruptions terminated the first explosive cycle of Santorini (Fig 1). They have been dated at 184 and 172 ka, respectively, by correlation with deep-sea ash layers (V-3 and V-1, respectively; Keller et al., 2000; Schwarz, 2000); for LP1 this is consistent with the previously published K-Ar age of 203 ± 24 ka
The LP1 eruption began with a Plinian phase, generating a pumice fall deposit up to 5 m thick. This was followed by discharge of pyroclastic flows, which laid down lithic lag breccia and ignimbrite up to 14 m thick. The products of LP1 are mainly rhyodacitic, but the eruption ended with the venting of a smaller quantity of andesite (Druitt et al., 1999). LP2 directly overlies LP1, separated by a palaeosol. The LP2 eruption began with a Plinian phase that laid down a pumice fall deposit up to 25 m thick. This was followed by pyroclastic flows and caldera collapse (‘caldera 1’; Fig. 1). The products of LP2 are uniformly rhyodacitic apart from the Plinian deposit, which also contains scoria of basaltic to andesitic composition (Druitt et al., 1999; Gertisser et al., 2009).

The second explosive cycle culminated with the Cape Riva (CR) and Minoan eruptions (Fig. 1). The dacitic CR eruption began with a Plinian phase, the pumice fall deposit of which is compositionally zoned, with subordinate andesitic and banded pumices in its upper half. At the end of the Plinian phase, the eruption column collapsed yielding a welded ignimbrite. The eruption then escalated violently; pyroclastic flows were discharged all over the islands and a caldera collapsed (‘caldera 3’, collapse of the Skaros-Therasia edifice; Druitt & Francaviglia, 1992). The eruption has been dated at 22 ka (Wulf et al., 2002; Fabbro et al., 2013). The Minoan eruption (3.6 ka) began with a Plinian phase (phase 1). The pumice fall deposit contains a predominant rhyodacitic component and two andesitic components, whose abundances increasing up sequence: (1) cauliflower andesitic enclaves and (2) a microphenocryst-rich andesitic pumice (Druitt et al., 1999; Druitt, 2014). Subsequent access of sea water to the vent initiated violent phreatomagmatic explosions and the emplacement of base surge deposits (phase 2) overlain by massive tuff (phase 3) which are interpreted as the products of low temperature (≤ 300°C), three-phase (solid, liquid, gas) pyroclastic flows (Sparks & Wilson, 1990). During the last phase of the eruption (phase 4), hot (300-350°C) pyroclastic flows were discharged and a caldera collapsed (‘caldera 4’, Fig. 1).
PREVIOUS CONSTRAINTS ON THE PRE-ERUPTIVE CONDITIONS

Pre-eruptive magma storage conditions have been determined previously for the Minoan and the Lower Pumice 2 eruptions. Experimental constraints exist only for the Minoan eruption (Cottrell et al., 1999). No such constraints exist so far for the Cape Riva and Lower Pumice 1 eruptions.

Minoan rhyodacite pre-eruptive constraints

Using coexisting ilmenite-magnetite pairs, Sigurdsson et al. (1990) estimated a pre-eruptive temperature for the Minoan rhyodacitic magma of 850°C and an oxygen fugacity ($f_{O2}$) of $10^{13}$, close to the Ni-NiO (NNO) buffer. More recent studies have confirmed this first estimate: Druitt et al. (2012) found a temperature of $853 \pm 12°C$ (Stormer, 1983; Anderson & Lindsley, 1985) while Cottrell et al. (1999) report a slightly higher temperature, $885 \pm 7°C$ at an $f_{O2}$ of $10^{11.7 \pm 0.2}$ (i.e., ~ NNO+0.5; Stormer, 1983; Anderson & Lindsley, 1988).

Pre-eruptive Minoan volatiles contents were determined by analysis of melt inclusions (MI) in plagioclase phenocrysts (Devine et al., 1984; Sigurdsson et al., 1990; Gardner et al., 1996; Cottrell et al., 1999; Michaud et al., 2000). These studies yield water contents ranging from 3.5 to 6.5 wt%. No data exist for CO$_2$ content. Chlorine is the most abundant volatile phase after water, with contents of 2800-3200 ppm (Devine et al., 1984; Cottrell et al., 1999; Michaud et al., 2000) whilst sulphur contents do not exceed 100 ppm (Sigurdsson et al., 1990; Cottrell et al., 1999; Michaud et al., 2000). Cottrell et al. (1999) reported fluorine and boron contents of 685-910 ppm and 16-25 ppm, respectively.

According to Sigurdsson et al. (1990), the water pressure of the rhyodacite magma prior to the Minoan eruption was 1.5–2.5 kbar. The magma was probably water-undersaturated with a total pressure in the range 2.5 to 5 kbar, indicating a reservoir at 8 to 15 km depth.
Cottrell *et al.* (1999) conducted exclusively water-saturated phase equilibria experiments on Minoan rhyodacite pumice at temperatures ranging from 800 to 975°C, pressure varying from 50 MPa to 250 MPa, and redox conditions near the NNO buffer. According to these authors, the Minoan rhyodacite was first stored at pressures of > 200 MPa and T ~ 825°C, then, a few months prior to eruption, it moved to a shallower ~ 50 MPa storage region where it reached a higher temperature (885°C), owing to mafic magma input. On the basis of their hypothesis, the Minoan rhyodacite would have contained ~ 3 wt% H₂O in the shallow reservoir, and ~ 6 wt% H₂O in the deeper one.

**Lower Pumice 2 pre-eruptive constraints**

Based on a study of natural rocks, Gertisser *et al.* (2009) determined a pre-eruptive Fe-Ti temperature of LP2 rhyodacitic magma of 831 ± 12°C and an oxygen fugacity of $f_{O_2} = 10^{13.7 ± 0.2}$ (thermometer of Andersen *et al.*, 1993), which is slightly above the FMQ (Fayalite-Magnetite-Quartz) oxygen buffer. The H₂O content of some glass inclusions was determined by FTIR spectroscopy, yielding pre-eruptive melt water contents of ~ 4.5 wt. %. No CO₂ was detected in any of the analysed glass inclusions, suggesting that there is less than 50 ppm (FTIR detection limit) of dissolved CO₂. The average chlorine content of the inclusion and interstitial glasses are similar (2490 ± 530 ppm and 2630 ± 210 ppm, respectively), suggesting that chlorine had insufficient time to degas during eruption (Gertisser *et al.*, 2009). In contrast, part of the sulphur was degassed during eruption, since glass inclusion sulphur content (140 ± 50 ppm) is higher than that of the interstitial glass (80 ± 20 ppm). Finally, Gertisser *et al.* (2009) determined a pre-eruptive storage pressure of 4.3 kbar (i.e., ~ 16 km depth assuming a crustal density of 2.7 g/cm³), based on the Al content of scarce amphibole phenocrysts in the rhyodacitic pumice (using the aluminium-in-hornblende geobarometer of Johnson & Rutherford, 1989).
SAMPLES SELECTION AND EXPERIMENTAL TECHNIQUES

Sampling strategy, starting material composition and preparation

For each eruption, we collected pumice clasts from the base of the Plinian fall deposit, which represents the first eruption phase. This strategy allowed us: 1/ to ensure that only the purest silicic component was sampled (avoiding mixed components generally located in the upper levels of the pumice fall) and, 2/ to ascertain the storage conditions at the top of the reservoir. The selected natural silicic components of the four eruptions have broadly similar major elements compositions (Table 1): rhyodacites for the Minoan, LP2 and LP1 eruptions (‘dry’ SiO$_2$ = 68.7-70.6 wt%) and dacite for the Cape Riva (‘dry’ SiO$_2$ = 66.9 wt%). They share an identical mineral assemblage, in which plagioclase and orthopyroxene (the most abundant phases) are accompanied by clinopyroxene, ilmenite, magnetite, apatite and pyrrhotite (commonly as inclusions in pyroxenes). We did not observe any amphibole, although this phase has been reported to occur at trace levels in both the Minoan and the LP2 products (Cottrell et al., 1999; Gertisser et al., 2009). The LP1 and LP2 pumices are crystal-poor (1-3 wt% and 6-8 wt%, respectively), while the CR and Minoan pumices have crystallinities higher than 10 wt% (~ 20 and 10-15 wt%, respectively; Electronic Appendix 6).

The whole rocks were crushed in an agate mortar and about 10 g of the resulting powders were melted twice, to ensure homogenization, at 1400°C and 1 atm. for 3-4 hours in a Pt crucible opened to air, then quenched. The dry glass thus obtained was analysed by electron microprobe ( Cameca SX 50, BRGM-ISTO, Orléans) with a sample current of 6 nA, an acceleration voltage of 15 kV and a defocused beam (5-6 μm). It was found to be similar to that of the whole-rock composition, except for a small depletion (< 0.8 wt%, Table 1) in Na$_2$O content. The glass was then reduced to powder and used as starting material for the experiments.
Choice of experimental conditions and general experimental strategy

The choice of experimental P, T, $X_{H_2O}, f_{O_2}$ conditions was guided both by our study of the natural samples and by the results of previous investigations (e.g., Cottrell et al., 1999; Gertisser et al., 2009). Our analyses of natural ilmenite-magnetite pairs indicate pre-eruptive temperatures ranging from ca. 850°C to 900°C (Table 2 & Fig. 2). The formulation of Ghiorso & Evans (2008) gives higher temperatures (+9 - 13°C) and lower $f_{O_2}$ (up to 0.5 log $f_{O_2}$) than those obtained using the calculation scheme of Stormer (1983) with the algorithm of Andersen & Lindsley (1985) (ILMAT software, Lepage, 2003). Hereafter, we will refer to the temperatures and oxygen fugacities calculated from Stormer (1983) and Andersen & Lindsley (1985) because their formulation gives the best agreement with data from phase equilibria experiments within the 850–900°C temperature range (Fig. 13 in Blundy & Cashman, 2008). Pre-eruptive temperatures are: 853 ± 7°C for the Minoan rhyodacite, 879 ± 15°C for the Cape Riva dacite, 856 ± 16°C for the Lower Pumice 2 rhyodacite and 869 ± 20°C for the Lower Pumice 1 rhyodacite. Redox conditions are close to FMQ (i.e., NNO-0.7) for CR, LP2 and LP1 (mean log $f_{O_2} = -12.92$ to -13.45), while the Minoan oxides record more oxidizing conditions, close to NNO. This $f_{O_2}$ jump of almost one log unit from the pre-Minoan magmas to Minoan magma is a remarkable feature of Santorini’s recent magmatic evolution (Fig. 2). Our T-$f_{O_2}$ estimates are consistent with those of Sigurdsson et al. (1990) and Gertisser et al. (2009) for the Minoan and LP2, respectively (Fig. 2). We thus performed experiments at 850°C and 900°C with redox conditions close to FMQ (experiments #1 to 4) and close to NNO+1 (experiments #5 and 6; Table 3). We explored a wide range of $H_2O$ and $CO_2$ contents, with $X_{H_2O} [= molar H_2O/(H_2O+CO_2)]$ ranging from 1 (i.e., $H_2O$-saturated) to 0.6 (i.e., $H_2O$-undersaturated). Our study thus complements previous similar work by Cottrell et al (1999), who investigated $H_2O$-saturated conditions only. The investigated pressures were 4, 2 and 1 kbar according to the previous literature constraints (see section above).
Because of their comparable chemical compositions (Table 1) and their similar pre-eruption magmatic temperatures (850-900°C) at any investigated P-T-fO₂, we systematically ran the four compositions together for each experiment, so as to minimize experimental errors in P, T, and fO₂, and to produce an internally consistent database. This approach ensured that any differences in phase relationships or in phase compositions between the different starting compositions observed at the same P-T-fO₂ conditions, are most probably related to bulk compositional effects (see below).

**Charge preparation and experimental equipment**

Known amounts of CO₂ (added as silver oxalate), distilled H₂O, and ~30 mg of silicate powder were loaded into Au capsules (15 mm length, 2.5 mm internal diameter and 0.2 mm wall thickness), as described elsewhere (e.g., Scaillet et al., 1995; Martel et al., 1998; Di Carlo et al., 2010). All charges were H₂O+CO₂ fluid-saturated. The bulk volatile content (H₂O+CO₂) was maintained at 9-10 wt%, and the initial fluid/silicate weight ratio at ~ 0.1 (i.e., the H₂O+CO₂ mass was 3 mg for 30 mg of glass powder). Five different XH₂O values were explored for each composition (i.e., eruption), which led to five capsules per composition for each experiment (except for experiments #5 and #6; Table 3).

Crystallization experiments were performed at ISTO (Orléans) with an Internally-Heated Pressure Vessel (IHPV) oriented vertically and equipped with a molybdenum furnace. The pressurizing medium was a mixture of Ar and H₂, the Ar/H₂ ratio of which was fixed by sequential loading at room temperature, so as to reach the desired target fO₂ (Scaillet et al., 1992, 1995). One or two redox sensors capsules were run with the experimental charges in order to determine *a posteriori* the fO₂ prevailing during each experiment. The sensor consisted of two pellets of hand-pressed Co-Pd-CoO (for FMQ buffered experiments) or Ni-Pd-NiO (NNO experiments) powder loaded with ~3 μl of distilled water into Au capsules and
lined with ZrO$_2$ powder to prevent contamination from the capsule (Taylor et al., 1992; Pownceby & O’Neill, 1994).

Pressure was recorded by a transducer calibrated against a Heise–Bourdon tube gauge (uncertainty ± 20 bars), while temperature was recorded by two S-type thermocouples. The overall temperature uncertainty is ± 5 °C (Scaillet et al., 1992; Schmidt et al., 1995).

Runs were terminated by switching off the power supply, and subsequent drop quench. Upon quenching, the sample holder fell immediately into the coldest part of the vessel (~50°C), producing a total pressure increase of ~ 40 bars. Run durations varied between 5 to 7 days (Table 3). After each experiment, the capsules were first weighted to check for leaks and opened. For each charge about one half of the run product was mounted in epoxy resin and polished.

**ANALYTICAL TECHNIQUES AND CONDITIONS**

**Run Products**

A total of 91 charges were first analysed by scanning electron microscopy (JEOL WINSET JSM 6400, ISTO Orléans) for preliminary textural analysis and phase identification; BSE images were acquired with a current of 7 nA and an acceleration voltage of 20 kV. Experimental glasses, minerals and solid sensors were then analysed by electron microprobe (Cameca SX 50 BRGM-CNRS-University of Orléans shared facility, and Cameca SX100 of the ‘Laboratoire Magmas et Volcans’, Université Blaise Pascal, Clermont-Ferrand, France).

Glasses and crystals were analysed with a sample current of 6 nA and an acceleration voltage of 15 kV, counting time of 10 s on peak and background for all elements; Na and K were analysed first and a ZAF correction was applied. The beam size was 5 to 10 μm for glass analyses, whereas it was focused for mineral analyses. Interstitial glasses were analysed together with dacitic and rhyolitic glass internal standards (Pinatubo 1991 eruption; Scaillet &
Evans, 1999) containing 0, 2, 4 and 6 wt% H₂O as determined by Karl Fischer titration. These standards were used in order to correct the electron microprobe analyses for Na migration under the beam and to estimate the amount of water dissolved in the interstitial glass using a modification of the by-difference method (Table 3; Devine et al., 1995; Scaillet et al., 1995). Owing to their small grain size, microprobe analyses of the experimental Fe-Ti oxides free from contamination from interstitial glass were difficult to obtain; most of them were recalculated assuming a SiO₂ content (wt%) near zero. Yet, in several charges, Fe-Ti oxides could not be analysed because they were smaller than the electron microprobe beam size (< 2 μm), and the glass contamination was too high to allow approximate correction using SiO₂ content.

Analytical conditions for Co-Pd-CoO and Ni-Pd-NiO sensors analyses were 20 kV – 20 nA, 10 s on each peak and 5 s on the background, the standards used during acquisition were Co or Ni-Pd-FeS-Au.

The intrinsic fH₂ prevailing during each experiment was calculated from the dissociation reaction of water using the fO₂ retrieved from the sensor, as given by the composition of the metallic alloys (Taylor et al., 1992), the fugacity of pure water (fH₂O°) as given by Burnham et al. (1969), and the water dissociation constant of Robie et al. (1978). The fO₂-fH₂ values calculated in this way correspond to those of water-saturated charges. Then, the fO₂ of each water under-saturated charge was determined using the method of Scaillet & Evans (1999), in which the XH₂O of the charge is taken as a proxy for the prevailing fH₂O (the term fH₂O° is replaced by XH₂O*fH₂O°) (see also Di Carlo et al., 2010; Andújar & Scaillet, 2012a; Table 3). Such an approach calculates maximum fO₂ for each corresponding charge. An fO₂ decrease of 0.4 log units occurs when XH₂O decreases from 1 to 0.6, that is, redox conditions become slightly more reduced in water-undersaturated capsules (Table 3). Altogether, we estimate that reported fO₂ are accurate within ± 0.3 log units.
Analysis of natural products

Natural phase compositions and proportions are given in Electronic Appendices 5 and 6 (available for downloading from http://www.petrology.oxfordjournals.org). Major element compositions for the Minoan phenocrysts and glasses come from T. Druitt (unpublished data); it was completed for volatile measurements of the melt inclusions in the present study. Crystal and glass compositions for CR, LP2 and LP1 eruptions are from this study.

Plagioclase and pyroxene crystals were extracted from pumice clasts of CR, LP2 and LP1 and embedded in epoxy resin so as to expose the (010) face of plagioclase crystals and the (100) or (010) faces of pyroxene crystals. Then, they were polished and coated with carbon for SEM imagery and electron microprobe analysis.

Major elements, chlorine, fluorine and sulphur were analysed in interstitial glasses and phenocryst-hosted melt inclusions using a Cameca SX 100 electron microprobe (“Laboratoire et Magmas et Volcans”, Clermont-Ferrand, France) with a 15 kV accelerating voltage. Major elements analyses were performed using a defocused electron beam (5 - 20 µm diameter depending on melt inclusion size), a sample current of 2 - 8 nA and 10s counting time on-peak. Na, K and Si were analysed first.

Analyses of F, S, P and Cl were performed at 30 or 80 nA with a 5 to 20 µm defocused beam depending again on the melt inclusion size. Cl, S and P were analysed on a Large PET crystal, while F was analysed simultaneously on three TAP crystals allowing low detection limits. In order to minimize volatile loss, each analysis of a single point was divided into five iterative sequences separated by beam blanking with the Faraday cup (Moune et al., 2007). Thus, the total on-peak acquisition time was 25s for P, 50s for Cl and S and 300s for F. Detection limits for Cl, F and S were respectively: ~80 ppm, 200 ppm and 50 ppm. Measured contents of
fluorine and in particular sulphur are generally close to, or lower than, the detection limit (Electronic Appendix 5a).

In order to obtain high-precision mineral analyses, measurements were performed using a 15 kV accelerating voltage, a focused beam and currents of 30 nA and 50 nA for plagioclase and pyroxenes, respectively. Despite relatively high current values, no sodium loss was observed. Fe-Ti oxides were analysed with a focused beam at 15 nA and 15 kV.

H$_2$O, CO$_2$, Cl, F and S concentrations of melt inclusions were determined by Secondary Ion Mass Spectrometry ( Cameca IMS 1280, CRPG, Nancy, France) using a Cs$^+$ primary beam projected onto a 10 µm diameter spot in Köhler mode with a 4-5 nA intensity. The electron gun was used with a HV adjusted by limiting the H$^+$ emission below 1000 cps. The positive secondary ions were measured at a mass resolution of 8000 in order to get a full separation of $^{16}$OH$^-$ and $^{17}$O$^-$ with a 30 ± 10 eV energy filtering and by peak switching in ion counting mode. The acquisition cycles included the mass 11.8 for the background, $^{12}$C, $^{17}$O, $^{16}$OH, $^{19}$F, $^{18}$O and $^{29}$Si, $^{30}$Si, $^{32}$S, $^{35}$Cl. For each measurement, the sample was pre-sputtered for 1 minute, the beam position and the magnetic field checked automatically, and 12 cycles were acquired for 9 minutes. The CO$_2$, H$_2$O, F, S, and Cl concentrations were calculated using the C/Si$^-$, OH/Si$^-$, F/Si$^-$, S/Si$^-$ and Cl/Si$^-$ ratios, respectively, with the relative useful yield relative to Si being determined on MPI-DING, natural and experimental glasses: StHs6/80-G (andesite; Jochum et al., 2006), Ke-12 (rhyolite from Kenya; Mosbah et al., 1991) and BT2 628-5, -6 and -7 (Bishop Tuff rhyolites synthetized by B. Scaillet, H$_2$O and CO$_2$ FTIR measurements performed by A. Cadoux). In spite of careful cleaning and polishing of the crystals aiming at removing carbon coat, SIMS carbon signal pointed out contamination which made our C/Si$^-$ data unworkable. H$_2$O, Cl, F and S contents from SIMS measurements are reported in Table 4. There is close agreement between the Cl, F and S contents measured by EMP (Electronic Appendix 5a) and those measured by SIMS.
EXPERIMENTAL PHASE EQUILIBRIA

General observations

Experimental conditions and phases proportions are reported in Table 3. Phase proportions were calculated for each charge by mass balance using major element compositions of experimental glasses and crystals (Electronic Appendices 1 to 4, available for downloading from http://www.petrology.oxfordjournals.org). Run products include glass, amphibole, clinopyroxene, plagioclase, orthopyroxene, ilmenite, magnetite and vesicles with sizes and proportions varying with XH₂O, or with melt water content which, as estimated with the by-difference method, ranges from 2.5 up to 9.8 wt%. The presence of vesicles in almost all charges is taken as evidence of fluid saturation. Crystals have euhehdral to sub-euhedral shapes: in most charges their size is smaller than 20 μm, the larger crystals (up to 150 μm length) occurring generally in H₂O-saturated (XH₂O = 1) charges. Crystallinity varies from 0 to 58 wt%, depending on XH₂O. Plagioclase is the most abundant mineral phase at XH₂O = 0.7-0.6, with mass proportions varying from trace amounts up to 47 wt% at XH₂O = 0.6. Orthopyroxene is generally the second most abundant phase (up to 10 wt% at XH₂O = 0.6), being sometimes superseded by amphibole, the abundance of which reaches up to 14 wt% at XH₂O = 0.9. Glass, amphibole, clinopyroxene and Fe-Ti oxides are the dominant phases at H₂O-saturation (XH₂O = 1), whilst plagioclase and orthopyroxene occur at drier conditions, except at 1 kbar-NNO+1 where both minerals occur at H₂O-saturation (Table 3). At 900°C and H₂O-saturation, clinopyroxene is the liquidus phase at 2 and 4 kbar, except for the LP2 rhyodacite, the liquidus phase of which is orthopyroxene. In contrast, at 850°C and H₂O-saturation, amphibole is the dominant phase for Minoan, Cape Riva and LP2 compositions, at both 2 and 4 kbar and at FMQ and NNO+1, clinopyroxene being even absent in Cape Riva indicating that clinopyroxene and amphibole are in a reaction relationship as temperature
decreases in the water-rich part of the phase diagrams. For the LP1 rhyodacite clinopyroxene crystallized first in all the experiments, suggesting the amphibole stability field lies at temperatures lower than 850°C over the investigated pressure and \( fO_2 \) range. Above-liquidus charges were only produced in experiments at 900°C, and under water-rich conditions.

Fe-Ti oxides are mostly < 3 μm in size, which makes them very difficult to identify and analyze. Magnetite was not identified in any charge of the FMQ experiments (Table 3): although it cannot be ruled out that trace amounts may have been overlooked, we believe that the lack of magnetite more likely reflects the moderately reduced conditions imposed in our experiments. In contrast, magnetite was identified in the NNO+1 experiments, but no ilmenite was found, probably because of the relatively oxidizing conditions.

In the LP2 rhyodacite, clinopyroxene was not detected in any of the run products, whereas orthopyroxene was present in most of the LP2 charges. In contrast, clinopyroxene was an almost ubiquitous phase in the LP1 run products and orthopyroxene crystallized only at 2 kbar-850°C-FMQ and at \( XH_2O \leq 0.7 \) (Table 3). This is a remarkable feature considering the very similar bulk rock compositions of LP1 and LP2 (Table 1). It can be noticed that when both pyroxenes crystallize, their respective fields of stability generally overlap very little (e.g., Figs. 3b and 4). Orthopyroxene and plagioclase both crystallized at \( H_2O \)-saturation at 1 kbar-850°C and NNO+1. At this pressure, no clinopyroxene was detected except in the LP1 rhyodacite, which crystallized clinopyroxene at \( H_2O \)-saturation, as observed at 2 and 4 kbar (Table 3).

**Phase relationships**

Phase boundaries (Figs. 3-6) were first drawn on the basis of phase assemblages of run products and subsequently refined using phase proportions (Table 3). For each composition, phase equilibrium diagrams are shown at constant pressure (2 and 4 kbar) and \( fO_2 \) (FMQ) as a
function of \( \text{XH}_2\text{O} \) and of temperature (°C). For the Minoan, a phase diagram of pressure versus \( \text{XH}_2\text{O} \) at 850°C and \( f\text{O}_2 = \text{NNO}+1 \) is also presented (Fig. 3c). For the four compositions, the effect of increasing pressure from 2 to 4 kbar is to displace each mineral-in curve towards lower temperature and lower \( \text{XH}_2\text{O} \). Similarly, the main effect of an increase of \( f\text{O}_2 \) from FMQ to NNO+1 is the replacement of ilmenite by magnetite (Table 3).

**Minoan rhyodacite**

At 2 and 4 kbar (Fig. 3), clinopyroxene is the liquidus phase crystallizing near 900°C at \( \text{XH}_2\text{O} = 1 \) (i.e., \( \text{H}_2\text{O}_{\text{melt}} > 6 \text{ wt%} \)). Clinopyroxene reacts out at temperatures below 850°C at \( \text{H}_2\text{O}-\)saturation, and at slightly higher temperatures as \( \text{H}_2\text{O}_{\text{melt}} \) decreases (Fig. 3a). It is accompanied by amphibole at temperatures lower than ca. 875°C and \( \text{H}_2\text{O}_{\text{melt}} > 5 \text{ wt%} \). At 2 kbar, the stability field of amphibole is restricted to \( \text{XH}_2\text{O} = 0.9-1 \), while at 4 kbar it extends towards lower \( \text{XH}_2\text{O} \) (= 0.7). At 850°C and 4 kbar, the abundance of amphibole is higher at \( \text{XH}_2\text{O} = 0.9 \) (6.6 wt%) than at \( \text{H}_2\text{O}-\)saturation (2.2 wt%). Orthopyroxene occupies essentially the dry portion of the phase diagram: the back bending of its stability curve at low temperatures, at both 2 and 4 kbar, is inferred from previous detailed experimental work on similar intermediate to silicic magmas (Scaillet & Evans, 1999; Dall’Agnol et al., 1999; Klimm et al., 2003; Costa et al., 2004). At 2 kbar, both clinopyroxene and orthopyroxene coexist in several charges at 850°C and 900°C (Fig. 3). We did not observe these minerals together at 4 kbar (orthopyroxene is absent in the experiments at 900°C), yet, based on the 2 kbar observations, a narrow co-existence domain is suggested on the corresponding phase diagram between 875 and 850 °C and \( \text{XH}_2\text{O} = 0.7-0.8 \). At 2 and 4 kbar, plagioclase requires less than 4.5 wt% \( \text{H}_2\text{O}_{\text{melt}} \) to crystallize at 900°C, and about 5.2-6.3 wt% \( \text{H}_2\text{O}_{\text{melt}} \) at 850°C (including at NNO+1, Fig. 3c).
Ilmenite is only stable at temperatures lower than 900°C at both 2 and 4 kbar in the FMQ experiments (Table 3). Magnetite is present in all the run products of 850°C-NNO+1 experiments, both at 2 and 1 kbar, in the XH2O range explored (= 0.8 to 1).

At 850°C, 2 kbar and XH2O = 0.8-1, the main effect of a higher fO2 (NNO+1) on phase equilibria of the Minoan rhyodacite is to expand the stability field of amphibole to XH2O ≤ 0.8, in addition to the replacement of ilmenite by magnetite (see experiments #2 and #5; Table 3).

A partial isothermal(850°C)-polybaric section shows that at 1 kbar - 850°C - NNO+1, plagioclase and orthopyroxene occur at water-saturated conditions along with amphibole (~ 3 wt% H2O_melt) (Fig. 3c), clinopyroxene being absent. At this temperature, clinopyroxene is not stable below 1.5 kbar at H2O-saturation.

*Cape Riva dacite*

The phase equilibria of the Cape Riva (Fig. 4) broadly resemble those of the Minoan, except that the T-XH2O coordinates of any liquidus curve are different. At H2O-saturation (XH2O = 1), clinopyroxene is the liquidus phase, crystallizing slightly above 900°C. In contrast, at 850°C and H2O-saturation, only amphibole (± ilmenite) is found at either 2 or 4 kbar. As stated previously, this indicates that clinopyroxene and amphibole are in a reaction relationship as temperature decreases. At 2 kbar, the clinopyroxene stability field is restricted to temperatures of > 850°C, as well as to higher H2O_melt (> ~6 wt%), being replaced by both orthopyroxene and plagioclase as H2O_melt decreases. At 4 kbar, the clinopyroxene stability field extends towards lower H2O_melt, but is not stable at 850°C. The field of amphibole extends towards lower XH2O (= 0.6) at 4 kbar than at 2 kbar (= 0.8), though these XH2O correspond to essentially the same H2O_melt values (6 wt%). As observed for the Minoan at 4 kbar-850°C, amphibole abundance reaches its maximum (up to 14 wt% at 850°C - 2 kbar) at
XH₂O = 0.9, and not at H₂O-saturation. Whatever the pressure and temperature, plagioclase in Cape Riva magma appears before orthopyroxene. Plagioclase is the most abundant phase, with mass proportions increasing with decreasing XH₂O up to 47 wt% at 850°C - 2 kbar and XH₂O = 0.6. Ilmenite is almost ubiquitous over the P-T-XH₂O conditions explored, appearing after clinopyroxene or amphibole, depending on XH₂O.

Lower Pumice 2 rhyodacite

Except for the location of the plagioclase stability curve, which remains broadly the same (plagioclase being the dominant phase in the water-poor part of the diagrams), the phase equilibria of the Lower Pumice 2 rhyodacite (Fig. 5) differ significantly from those of the Minoan and Cape Riva magmas, in particular in the lack of clinopyroxene.

At 2 kbar – 900°C, ilmenite is the liquidus phase, crystallizing slightly below H₂O-saturation, while it is replaced by amphibole at lower temperatures. In contrast to the Minoan and Cape Riva, orthopyroxene always crystallizes before plagioclase, whatever the pressure and temperature, and it is stable even at H₂O-saturation at 850°C (Fig. 5 and Table 3).

At 4 kbar, the ilmenite curve is significantly shifted toward lower temperatures as compared to the 2 kbar field. Orthopyroxene is the liquidus phase up to XH₂O = 0.9, but is replaced by amphibole at higher H₂O_melt values (> 5 wt%) and lower temperatures (< ca. 875°C). Amphibole is not stable at 900°C, as also observed at 2 kbar.

At 2 kbar-850°C and H₂O-saturation, increasing fO₂ from FMQ to NNO+1.8 makes orthopyroxene unstable (Table 3). At 1 kbar-850°C-NNO+1.7, both plagioclase and orthopyroxene occur at H₂O-saturation (i.e., H₂O_melt = 3.4 wt%, Table 3).

Lower Pumice 1 rhyodacite
At 2 and 4 kbar (Fig. 6), clinopyroxene is the liquidus phase stable almost all over the explored P-T-XH2O conditions. At 4 kbar, its stability field is slightly smaller than at 2 kbar; the upper limit being displaced to XH2O < 1 at 900°C, and the lower limit being moved to temperatures > 850°C at XH2O < 0.7 (Fig. 6). The plagioclase stability field is similar to that of the Minoan, CR and LP2 phase diagrams. Amphibole was not detected in any of the run products but, by analogy with the other three compositions, is inferred to crystallize at T < 850°C. Ilmenite is ubiquitous at 2 kbar, while at 4 kbar it is stable only below 900°C. Low-Ca pyroxene (pigeonite) was identified at T = 850°C and XH2O ≤ 0.8, at 2 and 4 kbar in the FMQ experiments. At 1 kbar – 850°C –NNO+1.7, LP1 rhyodacite crystallizes plagioclase at H2O-saturation (H2O_melt = 3.2 wt%, Table 3) as in the three other compositions.

EXPERIMENTAL PHASE COMPOSITIONS

General observations

The following features are common to the four eruptions (Figs. 7 to 14):

1. The experimental glasses show systematic compositional variations with increased crystallization: at fixed P-T-fO2, decreasing XH2O (i.e., H2O_melt) produces an increase in SiO2 and K2O contents, and a decrease in Al2O3, FeO, MgO and CaO (Figs. 7 to 10).

2. The melts produced at 900°C are less SiO2- and K2O-rich than those produced at 850°C. Similarly, at a fixed temperature, the melts produced at higher pressure are less SiO2- and K2O-rich than those produced at lower pressure, owing to the increasing water solubility with increasing pressure and lower crystallinity of the run products. At fixed P and T, the effect of increasing fO2 from FMQ to NNO+1 is to produce melts richer in SiO2 and K2O (Figs. 7 to 10) and products richer in crystals (Figs. 11a, 12a, 13a, 14a).
(3) The melt H$_2$O content at saturation is similar for all compositions, varying between 3-4 wt% at 1 kbar, 6-8 wt% at 2 kbar, up to 9-10 wt% at 4 kbar, in agreement with solubility constraints of H$_2$O for silicic magmas (e.g., Newmann & Lowenstern, 2002).

(4) Crystallinity increases with decreasing XH$_2$O (Figs. 11a, 12a, 13a, 14a).

(5) Mineral compositions vary with intensive parameters (Figs. 11 to 14). The compositions of ferro-magnesian minerals (pyroxenes, amphiboles, Fe-Ti oxides) are strongly affected by fO$_2$ variations, while plagioclase composition is sensitive to temperature and H$_2$O$_{melt}$.

**Minoan rhyodacite**

*Interstitial glass*

In all analysed charges, the experimental Minoan glasses are homogeneous within analytical uncertainty (Electronic Appendix 1a). They have compositions ranging from rhyodacitic to rhyolitic (SiO$_2$ = 71.5-76.8 wt%), depending on the experimental parameters (T-P-fO$_2$-XH$_2$O; Fig. 7) as stated above. The glass water content (H$_2$O$_{melt}$) decreases with decreasing pressure: at H$_2$O-saturation (XH$_2$O = 1), it is estimated to be 7-8 wt% at 4 kbar-FMQ and 850-900°C (Table 3), close to 6 wt% at 2 kbar and 850-900°C (both at FMQ and NNO+1), and decreases to 3 wt% at 1 kbar – 850°C – NNO+1.7.

*Plagioclase*

The plagioclase compositions given in Electronic Appendix 1b are average analyses, selected on the basis of a total close to 100 wt% and on the correctness of the structural formula. The anorthite contents (An) range between An$_{24}$ and An$_{42}$. At fixed P and fO$_2$, the anorthite content generally decreases with falling XH$_2$O (i.e., H$_2$O$_{melt}$) and increases with increasing temperature from 850°C to 900°C (Fig. 11b). The effect of temperature and H$_2$O$_{melt}$ on
plagioclase composition is more important than that of the pressure, as also observed for the interstitial glass compositions (Fig. 7).

**Orthopyroxene**

Though corrected for glass contamination, a number of analyses of experimental Minoan orthopyroxenes (Electronic Appendix 1c) still contain some Al2O3 (up to 2.7 wt%), due to the very small size of the crystals (< 5 μm), particularly in charges with XH2O < 0.8. The wollastonite component ranges from 3 to 12 %; it tends to increase with XH2O (reaching pigeonite-like composition for XH2O < 0.8), variations with other experimental parameters being less apparent (Fig. 5c). However, the FeO*/MgO ratio (where FeO* is total Fe as FeO) is lower for the orthopyroxenes produced at fO2 = NNO+1 than for those crystallized under more reduced FMQ conditions (Fig. 11d).

**Clinopyroxene**

The wollastonite component of experimental Minoan clinopyroxenes (Electronic Appendix 1d) ranges from 29 to 47 %. At 900°C, the wollastonite contents are lower (29- 41%) than at 850°C (41-47%; Fig. 11e), being also positively correlated with H2O_melt. Increasing fO2 induces lower FeO*/MgO ratios (Fig. 11f), as also observed in orthopyroxene.

**Amphibole**

Amphibole crystallized in the Minoan charges (Electronic Appendix 1e) exclusively at 850°C, at 1, 2 and 4 kbar and fO2 = FMQ and NNO+1, but was not found at XH2O lower than 0.8. The Mg# [Mg/(Mg+Fe)*100] values reflect the effects both of H2O_melt content and fO2: they tend to decrease progressively with decreasing XH2O and are higher at fO2 = NNO+1 (Mg# =
65-72%) than at \( f_\text{O}_2 = \text{FMQ} \) (Mg# = 64-54%; Fig. 11h). The effect of pressure on amphibole composition is moderate.

**Fe-Ti oxides**

Fe–Ti oxides were observed exclusively in experiments performed at 850°C. FMQ runs crystallized only ilmenite while NNO+1 runs crystallized only magnetite (Table 3). The mole fraction of ilmenite (X Ilm) calculated from Stormer (1983) is 0.95-0.96 and the mole fraction of ulvöspinel (X Usp) for the magnetite is in the range 0.17-0.23 (Fig. 11g). X Ilm and X Usp both increase slightly with decreasing XH\(_2\)O.

**Cape Riva dacite**

**Interstitial glass**

Compositions of interstitial glasses in the Cape Riva run products (Electronic Appendix 2a) are rhyodacitic to rhyolitic (SiO\(_2\) = 68-76 wt%; Fig. 8). The glass water content decreases with decreasing pressure: at H\(_2\)O-saturation, it is estimated to be in the range 8.7-9.6 wt% at 4 kbar-FMQ and 850-900°C, and close to 7 wt% at 2 kbar and 850-900°C (both at FMQ and NNO+1), decreasing to 3.6 wt % at 1 kbar – 850°C – NNO+1.7 (Table 3).

**Plagioclase**

The anorthite contents of the experimental Cape Riva plagioclases range between An\(_{22}\) and An\(_{39}\) (Electronic Appendix 2b). At fixed P- f\( f_\text{O}_2 \), the anorthite component generally decreases with falling XH\(_2\)O (i.e., H\(_2\)O\(_\text{melt}\)), and increases with increasing temperature from 850°C to 900°C (Fig. 12b).

**Orthopyroxene**
The wollastonite component of the experimental Cape Riva orthopyroxenes ranges between 3 to 22% (Electronic Appendix 2c). From Figure 12c, no clear relationship can be established with XH$_2$O or any other experimental parameters. At fO$_2$ = FMQ, the FeO*/MgO ratio is higher for the orthopyroxenes produced at 850°C (1.7-3.0) than at 900°C (1.3-2.1) and, at fixed T, FeO*/MgO ratio is slightly higher at 2 kbar than at 4 kbar (Fig. 6d). Finally, the NNO+1 experiment produced the orthopyroxene with the lowest FeO*/MgO (= 0.65) and the lowest wollastonite content (Figs. 12c and 12d).

**Clinopyroxene**

With the Cape Riva dacitic magma, clinopyroxene (Electronic Appendix 2d) was produced exclusively in experiments performed at 900°C-FMQ in the pressure and XH$_2$O range explored (Table 3). For the same XH$_2$O (= 0.9-0.8), clinopyroxenes crystallized at 2 kbar have lower wollastonite contents (Wo$_{38-41}$) and higher FeO*/MgO ratios (1.05-1.12) than those crystallized at 4 kbar (Wo$_{41-42}$ and FeO*/MgO =0.85-0.94; Figs. 12e and 12f). The wollastonite content increases with XH$_2$O up to 0.9 (Fig. 12e).

**Amphibole**

As in the Minoan rhyodacite, Cape Riva experimental amphibole (Electronic Appendix 2e) crystallized exclusively at 850°C, and is stable down to XH$_2$O = 0.7 (H$_2$O$_{melt}$ = 5.8 wt%) at 4 kbar-FMQ (Table 3). The Mg# of the amphibole is affected by the H$_2$O$_{melt}$ content and pressure, but more importantly by the fO$_2$: it tends to decrease progressively with decreasing XH$_2$O, whilst it displays slightly higher values at lower pressure and significantly higher values in oxidizing conditions (NNO+1: Mg# = 69-73%) compared to relatively reduced conditions (at FMQ: Mg# = 54-44%; Fig. 12h).
Fe-Ti oxides

Fe–Ti oxides were produced in the Cape Riva magma in all experiments (Electronic Appendix 2f). The X Ilm of ilmenite (FMQ runs) is 0.93-0.98 and the X Usp for the magnetite (NNO+1 runs) is 0.19-0.20 (Fig. 12g).

Lower Pumice 2 rhyodacite

Interstitial glass

The composition of interstitial glasses in the LP2 experiments (Electronic Appendix 3a) is rhyodacitic to rhyolitic (SiO$_2$ = 69-75 wt%), depending on T-P-fO$_2$-XH$_2$O conditions (Fig. 9). The glass water content decreases with decreasing pressure: at H$_2$O-saturation, it is in the range 8.4-9.6 wt% at 4 kbar-FMQ and 850-900°C, and about 5.6 to 8.0 wt % at 2 kbar and 850-900°C (both at FMQ and NNO+1), and it decreases to 3.4 wt% at 1 kbar – 850°C – NNO+1 (Table 3).

Plagioclase

The anorthite content of the experimental LP2 plagioclases ranges between An$_{26}$ and An$_{44}$ (Electronic Appendix 3b). At fixed P, it generally falls with decreasing XH$_2$O (i.e., H$_2$O$_{melt}$) and increases with increasing temperature from 850°C to 900°C (Fig. 13b).

Orthopyroxene

The wollastonite component of the orthopyroxenes (Electronic Appendix 3c) ranges from 3 to 6 %. It tends to increase with decreasing XH$_2$O and pressure (Fig. 13c). At fO$_2$ = FMQ, the FeO*/MgO ratio is higher for those orthopyroxenes produced at 850°C (~1.4-2.6) than at 900°C (~1.1-2.0) and, at 900°C, the FeO*/MgO ratio is higher at P = 2 kbar than at P = 4 kbar. There is not significant effect of pressure at 850°C (Fig. 13d). Finally, the NNO+1
experiment produced the orthopyroxene with the lowest FeO*/MgO (= 0.66) at H2O-saturation (Fig. 13d).

**Amphibole**

As in the Minoan and Cape Riva compositions, LP2 experimental amphibole (Electronic Appendix 3e) crystallizes only at 850°C, and is stable down to XH2O = 0.8 (i.e., H2O_melt = 6.3 wt%) at 4 kbar-FMQ (Table 3). At H2O-saturation, the Mg# of the amphibole is significantly higher at NNO+1 (Mg# = 71-74) than at FMQ (Mg# = 53-60; Fig. 13f). The effect of decreasing H2O_melt content in lowering the Mg# can be seen at 4 kbar-FMQ (Fig. 13f).

**Fe-Ti oxides**

Fe–Ti oxides were produced in all our LP2 experiments (Electronic Appendix 3f). Ilmenite and magnetite have X Ilm (0.94-0.97) and X Usp (0.18-0.20), similar to those of the Fe–Ti oxides of the Minoan rhyodacite and Cape Riva dacite (Fig. 13e).

**Lower Pumice 1 rhyodacite**

**Interstitial glass**

The compositions of the LP1 experimental glasses are reported in Electronic Appendix 4a. They are rhyodacitic to rhyolitic (SiO2 = 69.7-73.5 wt%), depending on T-P-fO2-XH2O conditions (Fig. 10). The glass water content decreases with decreasing pressure: at H2O-saturation, it is estimated to be in the range 8-10 wt% at 4 kbar-FMQ and 850-900°C, and close to 7 wt% at 2 kbar and 850-900°C (both at FMQ and NNO+1), and it decreases to 3.2 wt % at 1 kbar – 850°C – NNO+1 (Table 3).

**Plagioclase**
The LP1 experimental plagioclases (Electronic Appendix 4b) display significantly lower anorthite contents ($\text{An}_{14-26}$) in comparison with those produced with the other three magmas under the same experimental conditions ($\text{An}_{22-44}$). The anorthite content generally decreases with falling $X\text{H}_2\text{O}$ (i.e., $\text{H}_2\text{O}_{\text{melt}}$) and increases with increasing temperature from 850°C to 900°C (Fig. 14b).

**Pigeonite**

Low-Ca pyroxene was rare among the LP1 experimental products and difficult to analyse. The average compositions are given in Electronic Appendix 4c. Pigeonite compositions were found at 2 and 4 kbar-850°C-FMQ. The wollastonite contents range between 11 and 25 % and tend to increase with decreasing $X\text{H}_2\text{O}$ (Fig. 14c). At fixed $X\text{H}_2\text{O}$, pyroxenes formed at 2 kbar show higher wollastonite content ($\text{Wo}_{14-23}$) and lower FeO*/MgO ratio (2.4-2.6) than those formed at 4 kbar ($\text{Wo}_{11-15}$; FeO*/MgO = 2.7-2.9; Figs. 14c and 14d).

**Clinopyroxene**

Clinopyroxene ($W\text{o}_{31-46}E\text{n}_{30-40}F\text{s}_{15-38}$) is a ubiquitous phase in the experimental products of LP1 rhyodacite (Table 3, Electronic Appendix 4d). As observed for the other three magmas, clinopyroxene crystallizing at the lowest temperature and pressure has lower wollastonite contents ($\text{Wo} < 39\%$) and higher FeO*/MgO ratios (= 1.2-2.1; Figs. 14e and 14f). Clinopyroxenes from the NNO+1 runs present the highest Wo content (45-46 %) at $\text{H}_2\text{O}$-saturation (Fig. 14e). The Wo content is positively correlated with $X\text{H}_2\text{O}$, except at 850°C – 4 kbar.

**Fe-Ti oxides**
Fe–Ti oxides are also ubiquitous phases in all experiments with the LP1 rhyodacite (Electronic Appendix 4f). X Ilm of ilmenite (0.95-0.97; FMQ runs) and X Usp of the magnetite (0.17-0.19; NNO+1 runs; Fig. 14g) are similar to those of the oxides produced with the other rhyodacites.

PHASE COMPOSITIONS IN THE NATURAL PRODUCTS

Mineral compositions

Both plagioclase and pyroxene phenocrysts in pyroclasts from the four eruptions display complex zoning patterns. For the purpose of this study, we focused our attention on the rim compositions of the phenocrysts as they are assumed to be in equilibrium with the pre-eruption melt. Plagioclase rims have an average composition ranging from An$_{35}$ to An$_{42}$ (Minoan: An$_{39±1}$, Cape Riva: An$_{38±1}$, Lower Pumice 2: An$_{35±4}$, Lower Pumice 1: An$_{42±3}$; Electronic appendix 5b) in agreement with the values reported by Druitt et al. (1999). A bytownite rim (An$_{87}$) belonging to a sieve-textured euhedral xenocryst was analysed in the LP1 rhyodacite (Electronic appendix 5b). The four eruptions also have similar orthopyroxene and clinopyroxene rim compositions: Wo$_{3}$En$_{50-57}$Fs$_{41-47}$ and Wo$_{40-43}$En$_{36-39}$Fs$_{19-23}$, respectively. The same observations can be made for ilmenite-magnetite compositions (X Ilm ~0.9 and X Usp = 0.4-0.5; Electronic appendix 5b).

Compositions of melts inclusions and interstitial glasses

Interstitial glasses and phenocrysts-hosted melt inclusions (in plagioclase, ortho- and clinopyroxene) have very similar compositions in terms of major and volatile elements (Electronic appendix 5a, Table 4). The glass compositions are rhyodacitic for the Cape Riva dacite and the Lower Pumices 1 and 2 (SiO$_2$ = 69.3-71.0 wt% for interstitial glasses and 70.0-71.4 wt% for melt inclusions), and rhyolitic for the Minoan (SiO$_2$ = 73.8 wt% for interstitial
glasses and 72.1 wt% for melt inclusions). Both interstitial glasses and melt inclusions are chlorine rich: ~2700 ppm and 2800 ppm in average, respectively, for Cape Riva, Lower Pumice 2 and Lower Pumice 1, and 2900 ppm (interstitial glass) up to 3500 ppm (melt inclusions) in average for the Minoan. Fluorine and sulphur are minor species, with contents in the range 500-800 ppm and 50-100 ppm, respectively. These values are comparable to the earlier data of Devine et al. (1984), Sigurdsson et al. (1990), Cottrell et al. (1999) and Michaud et al. (2000) for the Minoan eruption, and are also close to the values reported by Gertisser et al. (2009) for Lower Pumice 2, except for S contents, for which they report higher values, notably in MI (140 ± 50 ppm). It is to note that the S contents of the MI that we measured both by EMP (41 ± 12 ppm; Electronic Appendix 5a) and SIMS (50 ± 2 ppm; Table 4) are in agreement. Thus, LP2 melt inclusions are probably heterogeneous with respect to sulphur.

For the four eruptions, water contents of melt inclusions are mostly in the range 3-6 wt%. There is no significant difference of water content according to their location within a single crystal, nor between plagioclases and pyroxenes (Table 4). The few melt inclusions with water contents lower than 3 wt% most probably leaked (e.g., Lowenstern, 1995).

**DISCUSSION ABOUT PHASE EQUILIBRIA**

**Attainment of equilibrium conditions during the experiments**

Our experimental strategy is well known for favouring crystal nucleation in alumino-silicate glasses (Clemens & Wall, 1981; 1986; Pichavant, 1987) and the attainment of crystal-liquid equilibrium on laboratory time-scales (Pichavant et al., 2007). Previous work, in particular on haplogranite compositions (equivalent to high-silica rhyolites), has shown that the use of fine-grained dry glass as starting material promotes crystal nucleation, leading to the production of equant textures in crystal-bearing charges. Attainment of equilibrium in silica-rich liquids
using such a procedure has been rigorously demonstrated by performing reversals (e.g., Pichavant, 1987), which have shown that, within experimental error, such a protocol does not lead to any mislocation of liquidus curves specific to each mineral. Our compositions are significantly less silicic than haplogranite, and our study has focused primarily on near-liquidus conditions, in keeping with the crystal-poor character of the studied Santorini magmas (ca. 2 to 20 wt%). Both factors (less silicic and crystal-poor) imply that melt viscosity, and hence component diffusivities, are significantly lower than in the high-silica rhyolites for which crystal-liquid equilibrium has been demonstrated. This in turn suggests that crystal nucleation and growth should not have been a problem in our study. In support of this statement is the following additional evidence: (1) early work performed on andesite-dacite compositions (Martel et al., 1999) has shown that, when not drop-quenched, such compositions end up producing abundant quench minerals. This observation shows that the activation energy for crystal nucleation in intermediate to silicic hydrous magma is surmountable; (2) the crystal abundance varies regularly and smoothly as functions of T and H$_2$O$_{meh}$, suggesting that this parameter is tightly controlled by intensive variables and not affected by crystal nucleation kinetics; (3) the phase boundary curve shapes are as expected from first-order thermodynamic considerations: in particular, the freezing-point depression effect of water on plagioclase stability is manifest in the four phase diagrams; (4) the amphibole stability curves, although differing between the four compositions studied, are similar to those from previous experimental and theoretical studies (Rutherford et al., 1985; Gardner et al., 1995; Ghiorso, 1997; Scaillet & Evans, 1999; Dall’Agnol et al., 1999; Martel et al., 1999; Bogaerts et al., 2006). The stronger depression of liquidus temperature of oxide phases (ilmenite) relative to plagioclase as pressure increases has been also previously documented by Sisson and Grove (1993). The smooth variation of phase compositions with variations of intensive parameters (Figs. 8 to 15) also supports a close approximation to
equilibrium conditions. We conclude that the phase diagrams define the equilibrium topology for each magma composition immediately prior to eruption. Differences in phase relationships between the four magmas are attributed to subtle variations in bulk chemistry, as discussed further below.

**Comparison with previous phase equilibria**

Previously, the phase relationships of the Minoan rhyodacitic magma have been determined exclusively under water-saturated conditions (Cottrell et al., 1999); this constitutes one of the main differences with our experimental approach in which we explored both water-saturated and water-undersaturated conditions. At 1 kbar-850°C-NNO+1, Cottrell et al. (1999) predicted amphibole occurrence along with plagioclase, pyroxene and Fe-Ti oxides, which is in agreement with our findings except for the occurrence of clinopyroxene (Fig. 3c, Table 3). Differences between the two data sets appear at 2 kbar-850°C-NNO+1 and include orthopyroxene and plagioclase, which are not found at H₂O-saturation in our study (Table 3). As extensively discussed by Pichavant et al. (2007), these features may be related to the different experimental procedures employed in each study: use of gently crushed pumice (Cottrell et al., 1999) versus use of dry glass material (this study), the former allowing metastable persistence of pre-existing crystals (especially if large phenocrysts, and/or phases having slow melting kinetics, such as tectosilicates, are initially present). Apart from the Cottrell et al. (1999) work, there is no other experimental study available on rhyodacite compositions *sensu stricto*.

For the dacitic magma of Cape Riva, which is the least silicic of the four Santorini compositions, a comparison can be made with that of the Pinatubo dacite, which has 65.5 wt% SiO₂ (Scaillet & Evans, 1999). Such a comparison reveals the same general topological arrangement between amphibole, orthopyroxene and plagioclase, the latter being displaced
down-temperature by more than 50°C (at comparable H₂O_melt) in Cape Riva, a result of the lower bulk CaO content relative to Pinatubo dacite (3.00 vs. 4.82 wt%). Despite the higher CaO content of the Pinatubo magma, clinopyroxene is restricted to very dry conditions in this composition at 2 kbar, while it appears on the liquidus in Cape Riva. Gardner et al. (1995) reported similar findings on the Wn dacite from Mt. St Helens, which has a composition very close to that of Cape Riva, except for a lower Fe/Mg ratio. Although the experimental coverage of Gardner et al. (1995) does not allow a detailed comparison with our 2-4 kbar phase relationships, the main feature of interest is the lack of clinopyroxene in the Wn dacite, despite the bulk rock having a higher CaO content compared to Cape Riva (3.8 vs. 3.0 wt%). The latter fact illustrates that, although clearly an essential component for clinopyroxene crystallization in magmas, the absolute abundance of CaO does not simply correlate with the stability field of clinopyroxene (i.e., the more CaO, the larger the stability field of clinopyroxene). One obvious reason is that clinopyroxene is in competition with other Ca-bearing minerals, in particular plagioclase and amphibole.

One critical difference between the above rocks is their FeO/MgO content, which is lower in the Wn and Pinatubo dacites than in Cape Riva. We tentatively suggest that, in addition to CaO, such a ratio exerts a control on the stability field of pyroxenes in hydrous intermediate to silicic magmas, calcic pyroxenes being favored by higher FeO/MgO ratios, everything else being equal. This parameter is not the only one affecting pyroxene stability, however. Experiments at higher pressures on the Pinatubo dacite (Prouteau & Scaillet, 2003) have shown that, as pressure increases, clinopyroxene progressively replaces orthopyroxene as the main pyroxene on the liquidus. The same is observed on Cape Riva, in which the orthopyroxene stability field shrinks considerably when going from 2 to 4 kbar (Fig. 4), but also on the other compositions, which crystallize both pyroxenes (Minoan and LP1). Expansion of the clinopyroxene stability field (relative to orthopyroxene) at higher pressure
goes along with that of amphibole, both being accompanied by the decreased stability of plagioclase. This suggests that water complexation with melt components affects more the melt precursor species of plagioclase than those leading to amphibole/clinopyroxene crystallization. The fact that orthopyroxene stability increases with decreasing pressure in intermediate to silicic magmas is reminiscent of the expansion of the stability field of olivine (relative to clinopyroxene) documented at low pressure in basalt (e.g., Di Carlo et al., 2006). In the more felsic magmas olivine is replaced by orthopyroxene by virtue of the higher prevailing silica activity. Altogether (and to a first order), provided that compositional effects have been well circumvented, this suggests that occurrence of orthopyroxene in place of clinopyroxene is an indication of low pressure magma equilibration conditions, as exemplified by the case of the Minoan (Fig. 3c).

Comparison of phase relationships between Santorini magmas

The above comparisons illustrate how subtle compositional factors may affect phase relationships of magmas of similar compositions (e.g., rhyodacites) in a rather complex way. Comparison between the four Santorini compositions serves to illustrate this sensitivity, with the advantage that the phase equilibria were determined using the same procedure and synthesis conditions. Taking into account that our P-T-fO2-XH2O experimental conditions were rigorously the same for all four magmas, observed differences can only be attributed to compositional differences between the starting products (Table 1).

Except for the LP2 rhyodacite in which clinopyroxene did not crystallize, the main mineral phases present in the natural rocks were reproduced experimentally for the four compositions. However, their phase relationships show marked differences (Figs. 3 to 6). Such significant topological differences were not anticipated, in particular between the Minoan and LP2 which are very similar, both petrologically and geochemically (Druitt et al.,
This is illustrated on Figures 15A and 15B, which compare the equilibrium curves of each phase in the four compositions used in this work. Clearly, both plagioclase and amphibole liquidus curves are similar in shape and T-XH$_2$O coordinates, while curves for pyroxenes and ilmenite differ from each other more markedly. Differences in the location of the ilmenite stability field may be attributed primarily to variations in FeO and TiO$_2$ contents (see Table 1): the Minoan composition has the lowest FeO (2.85 wt%) and TiO$_2$ (0.45 wt%) contents and displays the smallest ilmenite stability field (Fig. 15), whereas in the Cape Riva composition, which has the highest FeO (4.35 wt%) and TiO$_2$ (0.68 wt%) contents, the ilmenite stability field extends over all (at 2 kbar, Fig. 15A) or almost all (at 4 kbar, Fig. 15B) the phase diagram. Plagioclase systematics can be easily correlated with the variation in bulk CaO content, higher CaO producing higher plagioclase saturation temperatures at fixed H$_2$O$_{\text{melt}}$ (or XH$_2$O). The amphibole stability field also follows a similar rationale, its stability increasing with bulk CaO content (Figs. 15A and 15B). LP1 has the most extended clinopyroxene stability field both at 2 and 4 kbar (Figs. 15A and 15B), and this appears to be correlated with its higher FeO/MgO ratio (4.48) and lower CaO content (2.03 wt%) than those of the Minoan and Cape Riva, the clinopyroxene fields of which are smaller. The lack of clinopyroxene in LP2 is a case in point. The fact that this mineral has not been identified in both 2 and 4 kbar runs makes it difficult to propose phase overlooking as a possible explanation and strongly suggests instead that this is an intrinsic feature of LP2 phase equilibria (leaving aside nucleation problems as discussed previously). LP2 has the second highest FeO/MgO (4.24) after LP1 (FeO/MgO = 4.48), and a slightly higher CaO content (2.30 wt%, comparable to the Minoan; Table 1), which could favor clinopyroxene crystallization. The fact that this is not observed suggests that another compositional factor plays a role. Indeed, the stability fields of pyroxenes cannot be related in any simple way to the variation of a given major oxide. Instead, pyroxene stabilities result from the complex
interplay of several elements in particular Ca, Fe, Mg, Na and H$_2$O, or parameters such as pressure or $f$O$_2$, the individual and additive effects of which remain to be unraveled. It is remarkable that LP1, despite having the lowest CaO content of all of the four magmas, is the one in which clinopyroxene displays the largest stability field at either 2 or 4 kbar. This goes along with the smallest inferred stability field for amphibole (and plagioclase), both features indicating that amphibole and clinopyroxene are fundamentally in a reaction relationship as previously observed in silicic magmas (e.g., Dall’Agnol et al., 1999).

In summary, the systematics revealed by the four phase diagrams show that the variations of stability fields of alumino-silicate minerals (plagioclase and amphibole) in broadly chemically similar magmas can be reasonably explained with the use of simple melt “descriptors”, such as bulk CaO content in the present case. Conversely, it appears that silicate phases lacking aluminium as an essential component (pyroxenes) have stability fields that vary in a complex, and so far unpredictable, way, underlining the need for a more detailed knowledge of the atomic structures of hydrous natural multicomponent silicate melts.

**CONSTRAINTS ON PRE-ERUPTIVE CONDITIONS**

**Phase equilibrium constraints**

The phase relationships discussed above can be now used to set constraints on pre-eruption conditions, using the fact that the mineral assemblage Plg-Opx-Cpx-Fe-Ti oxide is common to the four compositions. First order constraints on temperature are provided by the fact that clinopyroxene reacts out generally below 850°C regardless of pressure and water content (Figs. 3-4), except in LP1 in which it is stable down to 800°C (Fig. 6). Clinopyroxene is replaced below 850-800°C by either amphibole (in water-rich conditions) or plagioclase (water-poor conditions). Orthopyroxene is generally not stable at H$_2$O-saturation in the pressure range 2-4 kbar: hence its occurrence indicates water-undersaturated conditions with
XH₂O < 0.9, corresponding to H₂O_melt generally lower than 6 wt% (Figs. 3-6), except for LP2 where water-saturation cannot be excluded using this sole criteria. Similarly, the lack of amphibole in the phenocryst assemblage of the four compositions points either to a pre-eruptive temperature higher than ca. 875°C or to H₂O_melt lower than 6 wt% (Figs. 3-6). The use of topological arguments alone provides no basis for a pressure estimate, which is equivalent to saying that there is no particular problem in reproducing the canonical phase assemblage at either 2 or 4 kbar.

Further insight can be gained by combining phase relationships with temperature constraints obtained from Fe-Ti oxides (Table 2), the different estimates of each rock being represented on Figs. 3-6 as grey bands. In all cases, upper and lower bounds on H₂O_melt are provided by plagioclase precipitation and its coexistence with pyroxenes, respectively. We first carry out such an analysis at 2 kbar, a possible long standing reservoir pressure for felsic eruptions as shown by Cottrell et al. (1999). For the Minoan magma, the H₂O_melt is in the range 5.2-6.3 wt% for a pre-eruptive temperature of 850°C (Fig. 3a), which fits well with melt inclusion analyses of this study (H₂O_melt = 4.0-5.8 wt%; Table 4) and those of Cottrell et al. (1999) (H₂O_melt = 3.5-6.5 wt%). The Cape Riva magma has a higher Fe-Ti oxide temperature, a slightly larger Plg stability field, and a restricted Cpx-Opx coexistence domain, which all combine to set an H₂O_melt value centered at 6.1 wt% (Fig. 4a). For the LP2 magma, the H₂O_melt cannot be higher than approximately 6 wt% at 865°C, which also agrees both with our SIMS measurements (H₂O_melt = 3.2-5.3 wt%; Table 4) and the FTIR measurements of Gertisser et al. (2009) (H₂O_melt = 4.5 wt%). The occurrence of clinopyroxene in LP2 pumices may be, to a first approximation, explained as resulting from admixing of crystals from invading mafic magmas, which also provided calcic plagioclase and olivine (Gertisser et al., 2009). Finally, LP1 requires an H₂O_melt of about 5 wt% at 865°C, which is best constrained by the stability field of orthopyroxene. Increasing pressure to 4 kbar does not significantly
change the above figures except for Cape Riva, which would require somewhat drier conditions, around 2.6 wt% H$_2$O$_{\text{melt}}$ (Fig. 4b). Therefore, if stored at 2 kbar, Santorini silicic magmas seem to achieve dissolved water contents in the range 4-6 wt% prior to eruption, pre-eruptive temperatures falling in a rather small temperature interval, 850-900°C.

While the natural mineral assemblages are broadly reproduced in the conditions explored, the absence of magnetite (which co-exists with ilmenite in the natural rocks) in the FMQ run products indicates that experiments were more reduced than the natural system. Conversely, the absence of ilmenite in the NNO+1 charges illustrates that the natural system is less oxidizing. It is concluded that the pre-eruptive redox states of the magmas lay between around FMQ and NNO+1, in agreement with Fe-Ti oxide constraints discussed earlier (Fig. 2, Table 2).

**Melt inclusion constraints**

The water contents measured in the melt inclusions (Table 4) indicate minimum trapping pressures (calculated from Newman & Lowenstern, 2002) ranging from 1.0 to 2.4 kbar for the four eruptions (considering the average and the highest H$_2$O for each eruption; Table 5): 1.3-2.0 kbar for the Minoan, 1.6-2.4 kbar for the Cape Riva, 1.0-1.7 kbar for the LP2 and, 1.3-2.2 kbar for the LP1. As some of the melt inclusions may have lost water, the highest values are probably the most meaningful (e.g., Lowenstern, 1995; Wallace, 2005). Chlorine contents, mostly between 2300 and 3500 ppm, are among the highest contents reported in the literature for silicic arc magmas (e.g., Lowenstern, 1995, Webster, 1997a; Wallace, 2005). It is noteworthy that such contents are similar to those found for Cl saturation (i.e., brine saturation) in many experimental investigations of silicic liquids at 2 kbar (i.e., 2600-3000 ppm; Webster & Holloway, 1988; Malinin *et al.*, 1989; Metrich & Rutherford, 1992; Webster, 1992a, 1992b, 1997b). On a diagram of chlorine (ppm) versus H$_2$O (wt%) (Fig. 16), the
Santorini data show that whatever the amount of dissolved water in the trapped melt, chlorine remains approximately constant, illustrating the contrasted behavior between chlorine and water (e.g., Webster, 1997a; Lowenstern, 2000). Melt inclusion data mainly fall on or above the H$_2$O-Cl (brine) saturation curve of the haplogranitic melts at 2 kbar (Webster, 1997a, 1997b), the offset being likely due to slightly higher Cl solubility of the Fe-natural melts as opposed to those Fe-free synthetics used in most experiments. This supports our assumption of considering the highest H$_2$O values as representative, i.e., the maximum H$_2$O-saturation pressure estimates of 1.7-2.4 kbar rather than 1.0-1.6 kbar (Table 5). Such a Cl-H$_2$O pattern suggests that magmas could have been saturated with both a hydrosaline liquid (brine) and a H$_2$O-Cl vapor prior to eruption (Fig. 16). In contrast to Cl, fluorine contents (~500-800 ppm) are comparable to those found in other silicic arc magmas (e.g., Lowenstern, 1995). Our unpublished data indicate that fluorine strongly partitions into apatite ($D_{F\text{apatite/melt}} = 35-44$, while $D_{Cl\text{apatite/melt}} = 2.8-3.6$; A. Cadoux et al., in preparation) which agrees very well with experimental results for felsic melts at 2 kbar and 900-924°C, saturated in brine ($D_{F\text{apatite/melt}} = 11-44$ and $D_{Cl\text{apatite/melt}} = 1.0-4.5$; Webster et al., 2009).

The low sulphur contents are common in silicic magmas in general. Because of strong temperature dependence of S solubility (e.g., Carroll & Webster, 1994; Scaillet et al., 2003), low temperature magmas like dacite and rhyolite have very low dissolved S (< 200 ppm and often < 60 ppm; Lowenstern, 1995). However, Santorini melts appear particularly depleted in sulphur when compared to the compositionally similar Krakatau dacite and rhyodacite magmas (Fig. 17a). The S contents of Santorini melts are comparable to silica-richer melts such as Pinatubo (SiO$_2$ ~76 wt%) or Katmai (SiO$_2$ ~77 wt%; Fig. 17a). It has been demonstrated that the maximum amount of S that can be dissolved in a silicate melt is controlled by saturation of the melt with a sulfide and/or a sulfate phase (e.g., Carroll and Rutherford, 1987; Luhr, 1990; Scaillet et al., 1998; Clemente et al., 2004), which is the case
for our Santorini silicic magmas, in which pyrrhotite globules are found in inclusions in pyroxenes and/or Fe-Ti oxides. The presence of this sulfide phase also provides additional evidence for the moderately reduced state of the system (e.g., Scaillet et al., 1998; Clemente et al., 2004). This reduced character may be at least partly at the origin of the very low sulphur contents in Santorini dacite and rhyodacites (Fig. 17c). It is unclear, however, if the low content of sulphur results from its degassing prior to melt inclusion entrapment, from sulphide disposal (i.e., settling) at early stages of magma fractionation, or from an intrinsically sulphur-poor system (i.e., sulphur-poor source), or from a combination of any of these mechanisms.

Comparison between natural and experimental phases compositions

Minoan rhyodacite

The natural bulk crystallinity and the composition of the interstitial glass are similar to those produced in the rhyodacite at a temperature of 850°C and a H$_2$O$_{melt}$ of about 5-6 wt% (0.7 < XH$_2$O < 1; Figs. 7 and 11a) at either 2 kbar (FMQ and NNO+1) or 4 kbar - FMQ. The natural clinopyroxene composition is also reproduced in these three experiments for XH$_2$O = 0.9-1.0 (Figs. 11e and 11f). The composition of the orthopyroxene is clearly not reproduced at a pressure of 4 kbar (Figs. 5c and 5d). Significantly, the compositions of the dominant phases in the natural product, plagioclase and orthopyroxene, are best reproduced at 850°C - 2 kbar – FMQ and H$_2$O$_{melt}$ = 6.3 wt% (XH$_2$O = 0.9; Figs. 11b to 11d). These temperature and water values are consistent with the temperature estimated from natural Fe-Ti oxides (Fig. 2; Table 2) and H$_2$O content measured in the melt inclusions (both in pyroxene and plagioclase, Table 4), respectively. The bulk crystallinity and phase proportions of the corresponding charge (9.7 wt%, Gl = 90.3, Plg = 6.9, Opx = 1.9, Cpx = 0.4, Ilm = 0.5 wt%; Table 3) are in close agreement with the natural product (10-15 wt%, Gl = 85.4, Plg = 11.2, Opx = 1.9, Cpx = 0.8,
Ilm = 0.4 wt%; Electronic Appendix 6). The mineral assemblage in the FMQ and NNO+1.8 runs (either ilmenite or magnetite, respectively), confirms that the $fO_2$ of the natural system lies between the two $fO_2$ explored, as also inferred from natural co-existing ilmenite and magnetite pairs (NNO-0.1; Fig. 2). Thus, combining natural and experimental constraints, we conclude that the pre-eruptive storage conditions of the Minoan rhyodacitic magma are: P ≥ 2 kbar, T = 853 ± 7°C, $H_2O_{melt} = 5-6$ wt%, Cl ~ 3500 ppm, F ~ 800 ppm, S ~100 ppm and $fO_2 = 10^{12.82 ± 0.19}$ (NNO-0.1).

Cape Riva dacite

Bulk crystallinity and interstitial glass compositions can be reproduced at 850°C, FMQ, 2 and 4 kbar and XH$_2$O ~0.9, as well as at 900°C, 2 kbar, FMQ for XH$_2$O = 0.7-0.8 (Figs. 8 and 12a). The run products of the 900°C - 4 kbar experiment reached neither the crystallinity nor the glass compositions of the natural pyroclast. The fact that clinopyroxene did not crystallize in any of the runs performed at T = 850°C (Table 3) indicates that the pre-eruptive temperature was > 850°C, which is in agreement with the temperature estimates from natural sample (879-909°C; Table 2). The natural clinopyroxene composition was reproduced in the runs performed at 900°C, 2 kbar, FMQ, XH$_2$O ~0.9 (Figs. 12e and 12f). Similarly, plagioclase composition is best reproduced at 900°C, 2 kbar, FMQ for XH$_2$O ~0.8 ($H_2O_{melt} = 6.1$ wt%). The same observation can be made for orthopyroxene in terms of FeO*/MgO ratio, although it does not match in terms of wollastonite content (Figs. 12c and 12d). Although there is no exact match, ilmenite composition is close to the natural one at 900°C, 2 kbar, FMQ at XH$_2$O = 0.8-0.9. As at XH$_2$O = 0.9, plagioclase and orthopyroxene are lacking in the mineral assemblage: hence XH$_2$O conditions were lower than 0.9 and higher than 0.7 (no Cpx at XH$_2$O = 0.7), which corresponds to $H_2O_{melt}$ comprised between 6.7 and 4.4 wt% (Table 3). This is consistent with melt inclusions data, as the majority has $H_2O_{melt}$ varying between 4.1
and 6.6 wt% (total average of ~5 wt%; Table 4). The absence of magnetite, which co-exists with ilmenite in the natural sample, reflects slightly more oxidizing conditions in the natural system as determined with ilmenite-magnetite pairs (log \( f_{O_2} = -12.92 \pm 0.35 \); i.e., NNO-0.7). Both natural and experimental products indicate that pre-eruptive storage conditions of the Cape Riva dacite magma are: \( P \geq 2 \) kbar, \( T = 879 \pm 15^\circ \text{C} \), \( H_2O_{\text{melt}}=5-6 \) wt\%, \( \text{Cl} \sim 2800 \) ppm, \( F \sim 800 \) ppm, \( S \sim 100 \) ppm and \( f_{O_2} = 10^{-12.92 \pm 0.35} \) (NNO-0.7).

Lower Pumice 2 rhyodacite

Bulk crystallinity and interstitial glass compositions can be both reproduced over most of the P-T-XH\(_2\)O explored, except in the NNO+1 runs. The composition of the main phase in the natural assemblage, plagioclase, is reproduced at 850°C both at 2 and 4 kbar for XH\(_2\)O ~ 0.7-0.8 (i.e., ~ 5.5 wt% H\(_2\)O\(_{\text{melt}}\) at 2 kbar and 4.6-5.1 wt% at 4 kbar; Table 3) but also at 900°C both at 2 and 4 kbar for lower XH\(_2\)O ~ 0.6-0.7 (i.e., ~ 3.5 wt% H\(_2\)O\(_{\text{melt}}\) at 2 kbar and 3.0 wt% at 4 kbar). However, at 900°C-2 kbar and XH\(_2\)O ~ 0.6-0.7, the crystallinity is too high in comparison with the natural one (respectively 14-18 wt% and 6-8 wt%; Table 3, Electronic appendix 6) excluding these as pre-eruptive conditions. The orthopyroxene composition is better reproduced in the 850°C (at 2 kbar and 4 kbar) runs at H\(_2\)O saturation (XH\(_2\)O = 1), than in the 900°C - 4 kbar run. The ilmenite composition is close to the natural one at 850°C, FMQ, at 2 and 4 kbar. These observations agree with a pre-eruptive temperature of about 850°C, which is consistent with the 856 ± 16°C temperature estimated from the natural Fe-Ti oxides pairs (Table 2). Both 2 kbar and 4 kbar can be considered as potential pre-eruptive pressures. However, in the considered XH\(_2\)O range (= 0.8-1.0) the main mineral assemblage and crystallinity at 4 kbar do not match: at XH\(_2\)O = 0.8, the assemblage has 2.7 wt% amphibole whereas it occurs rarely in the natural rock. At 2 kbar and XH\(_2\)O = 0.8, the bulk crystallinity (22.4 wt%) is significantly higher than the natural sample (6-8 wt%) while, at
H₂O saturation, the assemblage (3.3 wt% crystals) comprises 1.6 wt% amphibole, unlike the natural assemblage. In spite of lack of data at XH₂O = 0.9 (leakage of capsule), we can infer by extrapolation that the natural assemblage is produced at 850°C - 2 kbar - FMQ and XH₂O ~ 0.9 which corresponds to 5.5 < H₂Oₘₑˡᵗ < 8.0 wt%. This is broadly consistent with the highest measured H₂O content of 5.34 ± 0.54 wt% in melt inclusions (Table 4) which leads to a minimum pressure of 1.7 kbar (Table 5). Together with H₂O-Cl solubility constraints (Fig. 16), these data strongly support a 2 kbar, rather than 4 kbar, storage pressure. Thus, one may consider that the melt inclusions with H₂O < ~4.5 wt% (considering the error of the by-difference method of ±1 wt%) most likely underwent post-entrapment leakage. Although phase equilibrium experiments did not yield an exact natural mineral assemblage (absence of Cpx, discussed before), the composition of the main phases (glass, Plg and Opx) has been reproduced. Combining natural and experimental constraints, we thus conclude that the pre-eruptive storage conditions of the LP2 rhyodacitic magma are: P ≥ 2 kbar, T = 856 ± 16°C, H₂Oₘₑˡᵗ ~5-6 wt%, Cl ~ 2800 ppm, F ~ 800 ppm, S ~50 ppm and fO₂ = FMQ (10⁻¹³.₄₅ ± 0.₃₇; i.e., NNO-0.8).

Lower Pumice 1 rhyodacite

Both bulk crystallinity and interstitial glass compositions for LP1 are generally best reproduced in the products from experiments performed at T = 900°C in the XH₂O range = 0.8-1.0, at either 2 or 4 kbar. However, plagioclase did not crystallize at 4 kbar. It formed at 2 kbar but for lower XH₂O < 0.8 and overall, the composition of the experimental plagioclase is significantly less calcic (An < 28%) than the natural one in LP1 (An = 42%; Fig. 14b), and also less than the experimental plagioclases produced in the three other compositions (Figs. 11b, 12b, 13b), reflecting the higher Na and K contents of the starting bulk rock (Table 1). Orthopyroxene, the second most important phase of the natural rock, was not formed either;
instead, pigeonite crystallized in the 850°C - FMQ runs. This demonstrates that the orthopyroxene and the An₄₂ plagioclase cannot be in equilibrium with the LP1 rhyodacite. This is also supported by mass balance calculations which suggest that orthopyroxene and plagioclase are xenocrysts (Electronic Appendix 6). These latter have been most probably included in a LP1 clinopyroxene- and oxides-bearing silicic magma during a mixing event with a less evolved plagioclase- and orthopyroxene-bearing magma. The mixed system was not equilibrated at the time of eruption.

Despite this event, which prevents accurate experimental reconstruction of the pre-eruptive phase equilibria, one may still consider the constraints gained from the LP1 natural rhyodacite and its comparison with the products of the three other silicic eruptions, which show broadly similar phase assemblages and compositions. The minimum pressure estimates from melt inclusions are in the range 1.3-2.2 kbar (Table 5), pre-eruptive temperature and fO₂ are estimated to be 869 ± 20°C and ~ FMQ (10⁻¹³.₃₀ ± 0.₅₉ = NNO-0.₉, Table 2) and volatiles contents are very close to the Minoan, Cape Riva and Lower Pumice 2: maximum H₂Oₘₑₙt ~ 6.₃ wt% (mean H₂Oₘₑₙt = 4.₅ ± 0.₄ wt%), Cl ~ 2₈₀₀ ppm, F ~ ₉₀₀ ppm, S ~ ¹₀₀ ppm (Table 4).

**ON AMPHIBOLE OCCURRENCE AND ITS IMPLICATIONS**

**Minoan rhyodacite**

Phenocrystic amphibole is absent in the Minoan rhyodacite. However, Cottrell et al. (1999) suggested that amphibole should have crystallized on the basis of: (1) the high amount of water in the Minoan glass inclusions (up to 6.₅ wt%), and (2) previous experimental works on compositions similar to the Minoan rhyodacite which produced amphibole (e.g., Mount St Helens silicic rocks; Rutherford et al., 1985; Gardner et al., 1995).
The working hypothesis of those authors was thus that, if amphibole had crystallized at one time, its absence in the erupted rocks was due to a major change in the storage conditions prior to eruption. Cottrell et al. (1999) proposed a two stage equilibration model for the Minoan rhyodacitic magma. It was first stored at pressures > 2 kbar and T~ 825°C with ca. 6 wt% H₂O_melt; it then moved to a shallower ~ 0.5 kbar storage region with ca. 3 wt% H₂O_melt and a slightly higher temperature (885°C), owing to mafic magma input, during which amphibole phenocrysts reacted out.

Our phase equilibrium results show that such a change in storage conditions is not required to explain the absence of amphibole, for the following reasons:

1. Cottrell et al. (1999) based their experiments and interpretations on the assumption that the Minoan magma was water-saturated, which our new, mixed-volatile experiments do not support. Amphibole can be absent at 2 kbar and 850°C in a water-rich magma such as the Minoan if the magma is slightly water-undersaturated (XH₂O ~0.9).

2. They analysed melt inclusions in the cores (An₄₉₋₆₃) of plagioclase phenocrysts, but none in the rims (An₃₉±₂). Their model predicts that those in the rims should contain no more than 2.5-3.0 wt% H₂O (the saturation values at 0.5 kbar). However, we have analysed inclusions from both cores and rims (Table 4a) and find that both fall in the range 4-6 wt%, without any systematic difference. The rim inclusions commonly lie in deep re-entrants in the cores, where they are surrounded by thin shells of rim composition plagioclase. Water contents of melt inclusions in the rims (up to 4.65 wt%; Table 4a) are much higher than predicted by the model of Cottrell et al. (1999).

3. They reported the occurrence of rare iron-rich hornblende inclusions hosted by orthopyroxene grains, and used this as evidence that amphibole had been
previously stable in the magma at 2 kbar, but had reacted out when the magma moved to the last 0.5 kbar storage zone. While this is possible, we note that amphibole occurs abundantly in a suite of crystal-rich pumices that were co-erupted with the main rhyodacitic magma at the start of the Minoan eruption (Druitt et al., 1999). They represent parts of a highly crystalline intrusion that was partly pushed out by the ascending rhyodacite, with mingling between the two magmas (Druitt, 2014). Both the amphibole and host orthopyroxenes reported by Cottrell et al (1999) are compositionally very similar to those in the crystal-rich pumices (Fig. 18), raising the possibility that the orthopyroxene and its inclusion were introduced by syn-eruptive mingling into the rhyodacite, and have no bearing on the P-T-X evolution of the rhyodacite. It is notable that the crystal-rich magma appears to have been stored at a similar depth as the rhyodacite since the amphibole composition of the crystal-rich pumice yields pressure of 1.9 ± 0.5 kbar (Ridolfi et al., 2010).

In the present paper we argue that the phenocryst rim compositions, rim-hosted melt inclusion volatile contents, and the absence of phenocrystic amphibole in the Minoan rhyodacite form a sound basis for establishing a unique set of pre-eruptive conditions.

**Lower Pumice 2 rhyodacite**

Gertisser et al. (2009) reported rare amphibole as part of the crystal cargo of the LP2 rhyodacite, occurring either as phenocrysts, groundmass microlites or as crystals within melt inclusions. The authors used Al-in-hornblende geobarometry to estimate the depth of the storage region of the LP2 magma on the basis of:

1. The presence of rare quartz in the LP2 pumices
Assuming that the amphibole phenocrysts grew in equilibrium with quartz and the
tother phases in the LP2 rhyodacitic magma.

Amphibole phenocrysts of the LP2 pumices are described by Gertisser et al. (2009) as
generally unzoned, containing 10.4 ± 0.1 wt% Al$_2$O$_3$ (n=4), and yield a pressure of 4.3 ± 0.1
This corresponds to a depth of about 16 km, assuming a crustal density of 2.7 g/cm$^3$.
However, the LP2 magma clearly lacks the buffering assemblage needed for a proper use of
the Al-in-hornblende barometer as calibrated by Johnson & Rutherford (1989). Hence this
geobarometer cannot be used to infer the pre-eruptive magma storage pressure of the LP2
rhyodacite. Application of the more recent model of Ridolfi et al. (2010) yields a lower
pressure of 2.5 ± 0.6 kbar, a temperature of 931 ± 22°C and a H$_2$O$_{\text{melt}}$ content of 5.5 ± 0.8
wt%. Calculated pressure and melt H$_2$O content concur with our estimate of pre-eruptive
conditions (P ≥ 2 kbar, H$_2$O$_{\text{melt}}$ ~5-6 wt%). However, the calculated crystallization
temperature is high compared to our estimated value of 856 ± 16°C. This may reflect that the
amphibole crystals are antecrysts derived from less evolved magmas with higher
crystallization temperatures. The low Si content of the amphibole crystals (SiO$_2$ = 42 wt%;
Gertisser et al., 2009) compared to amphiboles of our experiments (SiO$_2$ = 44-47 wt%,
Electronic Appendix 3d) is consistent with such an interpretation.

SANTORINI MAGMA PLUMBING SYSTEM AND ITS EVOLUTION

Silicic magma storage regions

Our results show that the silicic magmas discharged during four large Plinian
eruptions of Santorini were stored under similar conditions immediately prior to eruption.
Considering a 2 kbar storage pressure and a crustal density of 2640 kg.m$^{-3}$ (Konstantinou,
2010), the top of the silicic magma storage regions is located at 7.7 km depth (i.e., in the
upper crust; Fig. 19). This storage pressure for silicic magmas is in agreement with recent phase equilibrium experiments on Santorini mafic and intermediate magmas, showing that andesitic magmas fractionate to dacite and rhyodacite at about 2 kbar (Andújar et al., 2012; Cadoux et al., 2013). Andesite comes from a deeper (~15 km) mafic storage region (Fig. 19), where basalts fractionate to basaltic andesite (55 to 58 wt% SiO$_2$) with 2-3 wt% H$_2$O at 1040-1000°C, 4 kbar and $f$O$_2$ = FMQ-0.5 (Andújar et al., 2012; Cadoux et al., 2013). Interestingly, even if it has to be further constrained, a similar scenario has been proposed for the earliest (~650 ka) rhyolitic magmas (early centres of Akrotiri, South of Thera Island, Fig. 1). Indeed, according to Mortazavi & Sparks (2004), Akrotiri differentiated mafic magma intruded into porphyritic silicic magma at depths of 7–10 km (water contents of the mafic magmas are estimated to have been > 4 wt% at water pressures of ≥ 1.8 kbar at temperatures of approximately 950–1000°C).

The similar P-T-volatile storage conditions, the closely spaced eruptive vents (Druitt et al., 1999) along with the large volumes (up to 30-60 km$^3$ DRE; Pyle, 1990; Sigurdsson et al., 1990; Druitt et al., 1999; Sigurdsson et al., 2006) of the silicic magmas discharged during the four large Plinian eruptions, suggest that they come from the same, presumably very large, reservoir. This hypothesis implies that this latter would have been sustained since at least 184 ka (the age of the Lower Pumice 1 eruption; Fig. 1), which is in agreement with recent thermal modelling (Gelman et al., 2013), that shows that an upper crustal reservoir can remain above its solidus for more than 100 ka when fed by magma fluxes typical of large magmatic provinces (i.e., < 0.005-0.008 km$^3$/year).

This ≥ 7.7 km reservoir depth beneath the caldera is close to that inferred for the 1650 AD rhyolite reservoir of the Kolumbo seamount, 6.5 km NE of Santorini (along the NE-SW trending Santorini-Kolumbo volcano-tectonic line; Fig. 19). The latter would be located around 6.8 km depth according to petrological, tomographic and stress field constraints
P- and S-wave tomographic images suggest that the current magma storage region is a small discrete reservoir, ca. 3 km diameter (Fig. 19; Dimitriadis et al., 2010; Konstantinou & Yeh, 2012).

**Size and shape of the silicic magma storage region**

Currently, there is no such geophysical evidence supporting the existence of a large storage region at ≥ 7.7 km beneath the Santorini caldera. However, this depth is comparable with that of emplacement of some granitoids of the Aegean Arc, such as the Miocene Tinos and Mykonos plutons emplaced at 10–12 km and at 5-10 km depth, respectively (e.g., Altherr et al., 1982; Buick, 1991; Lucas, 1999; de Saint-Blanquat et al., 2011) The total thicknesses of these plutons are approximately 1–2 km and 2-3 km, respectively, with volumes of 10-80 km$^3$ and ~ 150 km$^3$, respectively (Denèle et al., 2011; de Saint-Blanquat et al., 2011).

Reconstruction of the 3D shape of plutons from various tectonic settings has shown that the majority are tabular, wedge- or funnel-shaped (Scaillet et al., 1995; McCaffrey & Petford, 1997; Cruden, 1998; Vigneresse et al., 1999; Petford et al., 2000; Scaillet & Searle, 2006). On the basis of the positive correlation, evidenced by de Saint Blanquat et al. (2011), between pluton (s. l.) volume and the duration of its construction, we may infer that the final volume of the Santorini silicic storage region after 200 ka of growth might be in the range of 50-500 km$^3$, depending on the time-averaged construction rate, between ca. 0.001 and 0.01 km$^3$/yr, respectively (see Fig. 4 in de Saint-Blanquat et al., 2011). As the estimated magma volume discharged during the last large silicic Minoan eruption is up to 60 km$^3$ DRE (Sigurdsson et al., 2006), the storage region volume should be larger than 60 km$^3$. If we assume a tabular-shaped silicic storage region with an area of 65 km$^2$ (corresponding to the caldera area), its thickness could be comprised between 0.9 and 7.7 km (considering a volume of the storage region comprised between 60 and 500 km$^3$, respectively).
The volume of erupted Minoan magma could represent almost the totality (if the storage region is $\geq 60 \text{ km}^3$) to only 6% of the total volume of the storage region.

**Pre-eruptive magma storage variations**

Although magma storage conditions for the large silicic Plinian events do not appear to have changed since about 200 ka, some evidence suggests that they may have been different during the periods separating each of these Plinian eruptions. Interplinian phases at Santorini are characterized by effusive and minor explosive activity up to subplinian in intensity (Druitt *et al.*, 1999; Vespa *et al.*, 2006) and the products range from basalt to dacite in composition. Petrological studies of the post-Minoan, intra-caldera, Kameni dacitic lavas (197 BC to AD 1950) suggest that they were stored in a shallower region at a pressure of approximately 1 kbar (2-4 km in depth; Huijsmans, 1985; Barton & Huijsmans, 1986; Martin, 2005). This has supported the idea that the recent inflation of the caldera ground, the source of which has been estimated to be at 4.4 km depth (Newman *et al.*, 2012; Parks *et al.*, 2012), was due to magma intrusion. Therefore, even if pre-eruptive constraints are lacking for the oldest interplinian phases, it cannot be ruled out that variations in magma storage conditions of Santorini, such as those documented at Mt. St Helens and Vesuvius volcanoes (Gardner *et al.*, 1995; Rutherford & Devine, 2008; Scaillet *et al.*, 2008) have occurred in the past.

**CONCLUSIONS**

The systematic geochemical trends displayed by both experimental glass and minerals and their coherent variation with experimental variables (Figs. 7 to 14) show that conditions close to equilibrium were attained in our experiments. They were also broadly successful in reproducing the natural phase assemblages. Hence, the latter also approached equilibrium conditions prior to eruption (except Lower Pumice 1). Phase relationships show marked
differences between eruptions, in spite of their similar whole-rock compositions, due to the sensitivity of phase equilibria to small variations (< 1 wt%) in major element composition. This demonstrates how application of a phase diagram for a particular silicic magma might incorrectly predict phenocryst assemblages for another silicic magma. This point has also been made for phonolites (Scaillet et al., 2008; Andújar & Scaillet, 2012a), stressing the need for a case-by-case approach, whenever a precise estimate of pre-eruptive conditions is the chief objective of the experimental study.

Our results show that storage conditions prevailing before the four silicic Plinian eruptions of Santorini were similar and can be summarized as follows:

- T = 850°C – 900°C
- Moderately reduced conditions (ΔNNO = - 0.9 to - 0.1)
- Water-rich melts (~ 5-6 wt%)
- Sulphur depleted melts (≤ 100 ppm; buffered by pyrrhotite)
- Fluorine contents ~ 800 ppm, typical of silicic arc magmas
- Chlorine-rich melts (mostly between 2300 and 3500 ppm)
- Melts slightly undersaturated with respect to H2O, but most probably saturated with respect to H2O+Cl (± CO2) and a hydrosaline liquid.
- Storage pressure of 2 kbar or slightly more, but less than 4 kbar
- Reservoir roof depth at ≥ 7.7 km.

The Minoan silicic magma slightly differs from the Cape Riva and Lower Pumices by:

- Its slightly lower pre-eruptive temperature (consistent with its higher bulk dry SiO2; Tables 1 and 2)
- Its less reduced state (ΔNNO = - 0.1)
- Its higher chlorine content (3500 ppm in average, with maximum values > 4000 ppm)
We propose that Santorini magma plumbing system is dominated by a large, long-lived (≥ 200 ka) dominantly-silicic storage region at about 8 km depth (feeding the major Plinian eruptions; this study), which is maintained by mafic injections from a mafic reservoir at about 15 km depth (Andújar et al., 2012; Fig. 19).

Finally, the fact that Santorini silicic melts may have high enough dissolved Cl to be saturated in hydrosaline liquid has significant implications for the Cl degassing budget which will be treated in a separate article.
FUNDING
The present work was carried out in the framework of the project “Storage and Mixing at Santorini”, supported by the french “Agence Nationale de la Recherche” [ANR-08-BLAN-0249-01 to B.S.] and the Laboratoire d’Excellence VOLTAIRE (University of Orléans, France).

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REFERENCES


**FIGURE CAPTIONS**

**Figure 1.**
Cadoux et al., 2013

**Figure 1.**

- **a.** The sequence of the 12 major explosive eruptions of Santorini divided into two cycles (modified from Druitt *et al.*, 1999). White: dominantly silicic eruption, grey: dominantly andesitic eruption, black: interplinian eruption.
- **b.** Simplified geological map (slightly modified from Gertisser *et al.*, 2009).
**Figure 2.** Oxygen fugacity (log $f_O^2$) versus temperature (°C) calculated from Fe-Ti oxides from silicic pumices of the Minoan, Cape Riva, Lower Pumice 2 and Lower Pumice 1 eruptions (calculations performed with Stormer, 1983, and Andersen & Lindsley, 1985). All the ilmenite and magnetite pairs used for calculation are in equilibrium, according to their Mg/Mn ratios (Bacon & Hirschmann, 1988). They are touching and non-touching pairs included in the same pyroxene crystal or, touching pair in the groundmass. Previously published T - $f_O^2$ estimates for the Minoan (Sigurdsson et al., 1990; Cottrell et al., 1999) and the LP2 (Gertisser et al., 2009) eruptions are also shown. The FMQ and NNO oxygen fugacity curves were calculated for 2 and 4 kbar using Frost (1991).
(a) 2 kbar - FMQ

(b) 4 kbar - FMQ

(c) 850°C - NNO+1

Figure 3
Cadoux et al., 2013
**Figure 3.** Isobaric phase relationships of the Minoan rhyodacite at (a) 2 and (b) 4 kbar and FMQ as a function of $X_{H_2O}$ of the coexisting fluid phase and of temperature (°C). Curves are labeled with mineral names lying inside their stability fields. Plg = plagioclase, Opx = orthopyroxene, Cpx = clinopyroxene, Pig = pigeonite, A = amphibole, Ilm = ilmenite. Each black circle represents an experimental charge. Dark blue numbers: by-difference $H_{2O_melt}$ values in wt% (Table 3). Smaller italic black numbers are charge crystallinity in wt% (Table 3). Light grey dashed-lines indicate the anorthite content (%) of the experimental plagioclases (Electronic Appendix 1b). Grey band: pre-eruptive temperature range inferred from natural Fe-Ti oxides (Table 2). **3c.** Phase relationships at NNO+1 and 850°C as a function of $X_{H_2O}$ of the coexisting fluid phase and of pressure (kbar).
Figure 4. Isobaric phase relationships of the Cape Riva dacite at (a) 2 and (b) 4 kbar and FMQ as a function of X$_{H_2O}$ of the coexisting fluid phase and of temperature (°C). Same legend as Figure 3.
Figure 5. Isobaric phase relationships of the Lower Pumice 2 rhyodacite at (a) 2 and (b) 4 kbar and FMQ as a function of XH$_2$O of the coexisting fluid phase and of temperature (°C). Same legend as Figure 3.

Cadoux et al., 2013
Figure 6. Isobaric phase relationships of the Lower Pumice 1 rhyodacite at (a) 2 and (b) 4 kbar and FMQ as a function of XH$_2$O of the coexisting fluid phase and of temperature (°C). Same legend as Figure 3.
Figure 7. Experimental glass compositions of the Minoan rhyodacite as a function of \( \text{XH}_2\text{O} \).

The grey band is the composition of the natural interstitial glass and the vertical bar in the bottom left corner is the average standard deviation (wt\%) for the experimental glasses. Symbols: squares and diamonds are for 850\(^\circ\)C and 900\(^\circ\)C runs, respectively. Fill colour: white = 4 kbar, grey = 2 kbar and black = 1 kbar. White cross within the symbol indicates NNO+1 runs, no white cross means FMQ runs.
Figure 8. Experimental glasses composition of the Cape Riva dacite as a function of XH$_2$O.

Same legend as Figure 7.
Figure 9. Experimental glasses composition of the Lower Pumice 2 rhyodacite as a function of $XH_2O$. Same legend as Figure 7.
**Figure 10.** Experimental glasses composition of the Lower Pumice 1 rhyodacite as a function of XH$_2$O. Same legend as Figure 7.
Figure 11. Crystallinity and mineral compositions of the Minoan rhyodacite as a function of XH₂O. The composition of the natural phase is reported as a grey band or a black straight line.
Figure 12. Crystallinity and mineral compositions of the Cape Riva dacite as a function of XH$_2$O. Same legend as Figure 11.
Figure 13. Crystallinity and mineral compositions of the Lower Pumice 2 rhyodacite as a function of XH₂O. Same legend as Figure 11.
Figure 14. Crystallinity and mineral compositions of the Lower Pumice 1 rhyodacite as a function of XH$_2$O. Same legend as Figure 11.
Figure 15. Comparison of each mineral phase equilibria curve for the four compositions at the same experimental conditions. **A.** at 2 kbar - FMQ. **B.** at 4 kbar - FMQ. Values of melt “descriptors” discussed in the text (FeO, TiO₂, CaO, FeO/MgO, Na₂O) are reported.
Figure 16. Chlorine (ppm) versus H$_2$O (wt%) contents dissolved in melt inclusions of plagioclase and pyroxene phenocrysts from the Minoan, Cape Riva, Lower Pumice 2 and Lower Pumice 1 silicic magmas. They are compared with melt inclusions of other silicic arc magmas from Augustine and Katmai volcanoes (Alaska; Hildreth, 1983; Westrich et al., 1991; Hammer et al., 2002; Roman et al., 2006), Krakatau (Indonesia, Mandeville et al., 1996) and Pinatubo (Philippines, Gerlach et al., 1996). D and RD refer to the whole-rock composition: D = dacite, RD = rhyodacite.

The Cl-H$_2$O solubility curves at 0.5 and 2 kbar are taken from experimental data of Webster (1997b) for haplogranite liquids at 800 to 860°C. They suggest a trapping pressure equal or higher than 2 kbar. Vapor plus hydrosaline liquid exsolve at the point of intersection, i.e., the sharp break in curves slope (e.g., Webster, 2004).
**Figure 17.** Sulphur contents (ppm) of melt inclusions plotted against (a) dry SiO$_2$ (wt%), (b) pre-eruptive temperature (°C), (c) ΔNNO as indicator of redox state. Data sources for Santorini in Electronic Appendix 5a, for other volcanoes: same sources as in Fig.16 plus Scaillet & Evans (1999) for ΔNNO of Pinatubo dacite.
Figure 18. Amphibole compositions for the Minoan rhyodacite. (a) $\text{Al}_{\text{tot}}$ versus $\text{Mg}^\#$, (b) $\text{Mg}^\#$ versus $\text{Na+K}$ (per formula unit, on the basis of 23 oxygen). Experimental compositions are compared with the compositions of rare amphibole crystals found in the natural rhyodacite, as well as with those found in the Minoan crystal-rich pumices (data from Cottrell et al., 1999 and Druitt unpublished data, respectively).
Figure 19. Schematic interpretative illustration of the Santorini-Kolumbo magma plumbing system along a SW–NE cross-section from the Santorini caldera towards the Kolumbo seamount. Illustration based on the results obtained in this work, as well as recent volcanological, petrological and geophysical studies (see text). P-waves velocity variations beneath Kolumbo along with the hypocenter distribution (2002-2005 earthquakes) used in the tomography procedure of Dimitriadis et al. (2010) is shown. The seismicity is anti-correlated with the presence of the low-velocity areas, similar to what has been observed in other volcanic systems (e.g., De Natale et al., 2004). Sources for rheological limits and properties: Karagianni & Papazachos (2007), Endrun et al. (2008), Konstantinou (2010). White dashed...
ellipse represents the location of the negative velocity perturbation according to S-waves, which are believed to be more consistent than the location inferred from P-waves with petrological constraints (Konstantinou & Yeh, 2012).

There are at least four main magma storage regions beneath the Santorini-Kolumbo volcanic system: a mafic reservoir at 15 km depth (at the boundary between upper- and lower-crust; Andújar et al., 2012; Cadoux et al., 2013), a large dominantly-silicic reservoir at 8 km depth, a discrete smaller rhyolitic reservoir at ca. 7 km depth beneath Kolumbo (Dimitriadis et al., 2010; Cantner et al., 2014) and a shallower one at 2-4 km depth beneath the caldera (Parks et al., 2012 and references therein).

B = basalt, BA = basaltic andesite, A = Andesite, D = dacite, RD = rhyodacite, R = rhyolite.
Table 1. Whole rock and average double-fusion dry glass compositions of the four samples used as starting materials. All compositions have been recalculated to 100 wt% on an anhydrous basis. Except for the Minoan (XRF, Nottingham, UK), whole rock major element analyses were all performed at the SARM-CRPG (Nancy, France) by ICP-OES. FeO (Fe$^{2+}$) content was determined by wet chemistry, H$_2$O$^+$ with Karl Fisher potentiometric titration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minoan</th>
<th>CAPE RIVA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Whole Rock</td>
<td>Dry Glass (double fusion)</td>
</tr>
<tr>
<td>S82-30</td>
<td>70.58</td>
<td>71.24 (26)</td>
</tr>
<tr>
<td></td>
<td>0.46</td>
<td>0.45 (4)</td>
</tr>
<tr>
<td></td>
<td>14.64</td>
<td>14.87 (15)</td>
</tr>
<tr>
<td></td>
<td>n.a.</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.08 (5)</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>0.73 (5)</td>
</tr>
<tr>
<td></td>
<td>2.36</td>
<td>2.34 (14)</td>
</tr>
<tr>
<td></td>
<td>5.08</td>
<td>4.24 (8)</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>3.08 (11)</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.13 (4)</td>
</tr>
<tr>
<td></td>
<td>n.a.</td>
<td>H$_2$O$^+$</td>
</tr>
<tr>
<td></td>
<td>n.a.</td>
<td>H$_2$O$^+$</td>
</tr>
<tr>
<td></td>
<td>n.a.</td>
<td>S$_{tot}$</td>
</tr>
<tr>
<td></td>
<td>n.a.</td>
<td>CO$_{2tot}$</td>
</tr>
<tr>
<td></td>
<td>2.12</td>
<td>L.O.I</td>
</tr>
<tr>
<td></td>
<td>99.99</td>
<td>Original Sum</td>
</tr>
</tbody>
</table>


$n$ : number of dry glass analyses.

Numbers in parentheses indicate one standard deviation of $n$ analyses in terms of smallest units cited.
n.a.: not analysed
H₂O by gravimetry, CO₂tot and S₄ were measured with a Leco SC 144DR. Chlorine content was determined by wet precipitation- ferrithiocyanate spectrophotometry. Boron was measured using a Varian Cary 50 absorptiometry Spectrophotometer and Lithium by Atomic absorption spectroscopy. Dry glasses were analysed with a Cameca SX50 electron microprobe (ISTO-BRGM, France).

**Table 2. Mean pre-eruptive temperatures and oxygen fugacities**

<table>
<thead>
<tr>
<th></th>
<th>Minoan</th>
<th>Cape Riva</th>
<th>Lower Pumice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ti Oxides</td>
<td>T (°C) ± 1SD</td>
<td>log fO₂ ± 1SD</td>
<td>T (°C) ± 1SD</td>
</tr>
<tr>
<td>Andersen &amp; Lindsley (1985)</td>
<td>853 ± 7</td>
<td>-12.82 ± 0.19</td>
<td>879 ± 15</td>
</tr>
<tr>
<td>Ghiorso &amp; Evans (2008)</td>
<td>866 ± 9</td>
<td>-12.86 ± 0.07</td>
<td>891 ± 17</td>
</tr>
<tr>
<td>P solubility (apatite-melt)</td>
<td>Harrison &amp; Watson (1984)</td>
<td>807</td>
<td>909</td>
</tr>
</tbody>
</table>

**Table 2.** Mean pre-eruptive temperatures and oxygen fugacities. Temperature estimates from Fe-Ti oxides and P solubility are mostly consistent, showing that the less evolved Cape Riva magma is the hotter one. The calculation scheme of Ghiorso & Evans (2008) systematically leads to higher temperatures (+9 to 13°C) and lower fO₂ (up to 0.5 log fO₂) than Andersen & Lindsley (1985) but the two techniques agree within one standard deviation.
Table 3. Phase equilibria experiments: conditions, run products and phase proportions

<table>
<thead>
<tr>
<th>Charge #</th>
<th>Starting material</th>
<th>( \log f_\text{O}_2 )</th>
<th>( \text{XH}_2\text{O}^2 )</th>
<th>( \text{H}<em>2\text{O}</em>{\text{melt}} ) (wt%)</th>
<th>Run products and phase proportions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP2 I</td>
<td>dry glass</td>
<td>-12.29 ( \text{FMQ} + 0.2 )</td>
<td>1</td>
<td>5.6</td>
<td>Gl only</td>
</tr>
<tr>
<td>LP2 II</td>
<td></td>
<td>-12.38</td>
<td>0.9</td>
<td>5.2</td>
<td>Gl (99.0), Opx (0.8), Ilm (0.1)</td>
</tr>
<tr>
<td>LP2 III</td>
<td></td>
<td>-12.49</td>
<td>0.8</td>
<td>4.4</td>
<td>Gl (90.6), Plg (7.4), Opx (1.7), Ilm (0.1)</td>
</tr>
<tr>
<td>LP2 IV</td>
<td></td>
<td>-12.60</td>
<td>0.7</td>
<td>3.7</td>
<td>Gl (86.2), Plg (10.1), Opx (3.3), Ilm (0.4)</td>
</tr>
<tr>
<td>LP2 V</td>
<td></td>
<td>-12.74</td>
<td>0.6</td>
<td>3.3</td>
<td>Gl (81.9), Plg (14.0), Opx (3.8), Ilm (0.3)</td>
</tr>
<tr>
<td>LP1 VI</td>
<td></td>
<td>-12.29</td>
<td>1</td>
<td>7.1</td>
<td>Gl (98.1), Cpx (1.6), Ilm (0.3)</td>
</tr>
<tr>
<td>LP1 VII</td>
<td></td>
<td>-12.38</td>
<td>0.9</td>
<td>6.0</td>
<td>Gl (96.7), Cpx (2.9), Ilm (0.4)</td>
</tr>
<tr>
<td>LP1 VIII</td>
<td></td>
<td>-12.49</td>
<td>0.8</td>
<td>4.3</td>
<td>Gl (96.3), Cpx (3.3), Ilm (0.4)</td>
</tr>
<tr>
<td>LP1 IX</td>
<td></td>
<td>-12.60</td>
<td>0.7</td>
<td>4.2</td>
<td>Gl (92.8), Cpx (4.3), Plg (2.3), Ilm (0.3)</td>
</tr>
<tr>
<td>LP1 X</td>
<td></td>
<td>-12.74</td>
<td>0.6</td>
<td>4.1</td>
<td>Gl (85.2), Plg (8.6), Cpx (5.6), Ilm (0.3)</td>
</tr>
<tr>
<td>Min XI</td>
<td></td>
<td>-12.29</td>
<td>1</td>
<td>6.3</td>
<td>Gl only</td>
</tr>
<tr>
<td>Min XII</td>
<td></td>
<td>-12.38</td>
<td>0.9</td>
<td>5.8</td>
<td>Gl (97.0), Cpx (3)</td>
</tr>
<tr>
<td>Min XIII</td>
<td></td>
<td>-12.49</td>
<td>0.8</td>
<td>4.5</td>
<td>Gl (97.3), Cpx (2.2), Plg (0.5)</td>
</tr>
<tr>
<td>Min XIV</td>
<td></td>
<td>-12.60</td>
<td>0.7</td>
<td>3.9</td>
<td>Gl (91.5), Plg (6.5), Opx (2.9), Cpx (0.1)</td>
</tr>
<tr>
<td>Min XV</td>
<td></td>
<td>-12.74</td>
<td>0.6</td>
<td>3.5</td>
<td>Gl (83.4), Plg (13.2), Opx (4.3), Cpx (1.7)</td>
</tr>
<tr>
<td>CR XVI</td>
<td></td>
<td>-12.29</td>
<td>1</td>
<td>7.7</td>
<td>Gl (96.5), Cpx (3.1), Ilm (0.3)</td>
</tr>
<tr>
<td>CR XVII</td>
<td></td>
<td>-12.38</td>
<td>0.9</td>
<td>6.7</td>
<td>Gl (95.3), Cpx (4.0), Ilm (0.7)</td>
</tr>
<tr>
<td>CR XVIII</td>
<td></td>
<td>-12.49</td>
<td>0.8</td>
<td>6.1</td>
<td>Gl (88.7), Plg (5.5), Cpx (2.8), Opx (1.0)</td>
</tr>
<tr>
<td>CR XIX</td>
<td></td>
<td>-12.60</td>
<td>0.7</td>
<td>4.4</td>
<td>Gl (75.5), Plg (16.9), Opx (6.8), Ilm (0.7)</td>
</tr>
<tr>
<td>CR XX</td>
<td></td>
<td>-12.74</td>
<td>0.6</td>
<td>4.2</td>
<td>Gl (66.4), Plg (24.5), Opx (8.2), Ilm (0.7)</td>
</tr>
</tbody>
</table>

**Experiment # 1:** \( P_t = 2022 \pm 15 \text{ bar, } P_{H_2} = 5.8 \text{ bar (target: FMQ buffer), } T = 902 \pm 6^\circ\text{C}, \text{ run duration 164.8 hours} \)

**Experiment # 2:** \( P_t = 2004 \pm 12 \text{ bar, } P_{H_2} = 6 \text{ bar (target: FMQ buffer), } T = 850 \pm 1^\circ\text{C}, \text{ run duration 212.1 hours} \)

**Experiment # 3:** \( P_t = 4135 \pm 19 \text{ bar, } P_{H_2} = 6.6 \text{ bar (target: FMQ buffer), } T = 901 \pm 1^\circ\text{C}, \text{ run duration 126.1 hours} \)
Table 3. Phase equilibria experiments: conditions, run products and phase proportions.
### Table 4a. Volatile compositions of the Minoan melt inclusions (MI) from SIMS measurements

<table>
<thead>
<tr>
<th>Sample-Crystal#-MI#</th>
<th>Host</th>
<th>MI location</th>
<th>Dry SiO2</th>
<th>Touching Plg</th>
<th>H2O ±</th>
<th>Cl ±</th>
<th>F ±</th>
<th>S ±</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>wt%</td>
<td>An/wt%</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>S82-34B-A3 MI1/2</td>
<td>Plg</td>
<td>R</td>
<td>73.4</td>
<td>42.1</td>
<td>4.01</td>
<td>0.41</td>
<td>4183</td>
<td>130</td>
</tr>
<tr>
<td>S82-34B-A3 MI3</td>
<td>Plg</td>
<td>R</td>
<td>73.4</td>
<td>41.6</td>
<td>4.65</td>
<td>0.47</td>
<td>2991</td>
<td>244</td>
</tr>
<tr>
<td>S82-30A-B3 M14/4</td>
<td>Plg</td>
<td>C</td>
<td>72.4</td>
<td>50.2</td>
<td>5.82</td>
<td>0.58</td>
<td>4437</td>
<td>187</td>
</tr>
<tr>
<td>S82-30A-6 MI1/2</td>
<td>Plg</td>
<td>R</td>
<td>72.5</td>
<td>39.9</td>
<td>4.60</td>
<td>0.46</td>
<td>3500</td>
<td>112</td>
</tr>
<tr>
<td>S82-11D-A5 MI1/2</td>
<td>Plg</td>
<td>C</td>
<td>72.3</td>
<td>50.0</td>
<td>4.13</td>
<td>0.42</td>
<td>3144</td>
<td>156</td>
</tr>
<tr>
<td>S82-11D-A5 MI3</td>
<td>Plg</td>
<td>C</td>
<td>71.4</td>
<td>49.4</td>
<td>4.07</td>
<td>0.43</td>
<td>2817</td>
<td>134</td>
</tr>
</tbody>
</table>

*SiO2 used by default for water content calculation
n.a.: not analysed

### Table 4b. Volatile compositions of the Cape Riva melt inclusions (MI) from SIMS measurements

<table>
<thead>
<tr>
<th>Sample-Crystal#-MI#</th>
<th>Host</th>
<th>MI location</th>
<th>Dry SiO2</th>
<th>Touching Plg/Px</th>
<th>H2O ±</th>
<th>Cl ±</th>
<th>F ±</th>
<th>S ±</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>wt%</td>
<td>An/wt%</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>S09-62f-10 MI1</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.1</td>
<td>n.a.</td>
<td>5.27</td>
<td>0.13</td>
<td>2747</td>
<td>109</td>
</tr>
<tr>
<td>S09-62f-10 MI2</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.2</td>
<td>n.a.</td>
<td>4.74</td>
<td>0.16</td>
<td>2369</td>
<td>25</td>
</tr>
<tr>
<td>S09-62f-10 MI3</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.3</td>
<td>n.a.</td>
<td>5.13</td>
<td>0.47</td>
<td>2504</td>
<td>233</td>
</tr>
<tr>
<td>S09-62f-10 MI5</td>
<td>Plg</td>
<td>R</td>
<td>71.2</td>
<td>n.a.</td>
<td>4.95</td>
<td>0.51</td>
<td>2577</td>
<td>81</td>
</tr>
<tr>
<td>S09-62f-9 MI1</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.2</td>
<td>41.6</td>
<td>5.77</td>
<td>0.64</td>
<td>2711</td>
<td>143</td>
</tr>
<tr>
<td>S09-62f-9 MI2</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.9</td>
<td>41.5</td>
<td>3.65</td>
<td>0.42</td>
<td>2385</td>
<td>115</td>
</tr>
<tr>
<td>S09-62f-9 MI5</td>
<td>Plg</td>
<td>GR-RS</td>
<td>70.9</td>
<td>42.1</td>
<td>4.57</td>
<td>0.51</td>
<td>2805</td>
<td>151</td>
</tr>
<tr>
<td>S09-62f-2 MI1</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.6</td>
<td>42.7</td>
<td>4.11</td>
<td>0.41</td>
<td>2644</td>
<td>259</td>
</tr>
<tr>
<td>S09-62f-2 MI3</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.3</td>
<td>41.5</td>
<td>5.27</td>
<td>0.82</td>
<td>2912</td>
<td>299</td>
</tr>
<tr>
<td>S09-62h-6 MI1</td>
<td>Plg</td>
<td>GR-RS</td>
<td>71.2*</td>
<td>6.61</td>
<td>0.66</td>
<td>2451</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>S09-62c-2 MI1</td>
<td>Opx</td>
<td>C</td>
<td>71.4</td>
<td>n.a.</td>
<td>3.27</td>
<td>0.33</td>
<td>2793</td>
<td>99</td>
</tr>
<tr>
<td>S09-62c-2 MI2</td>
<td>Opx</td>
<td>C</td>
<td>71.0</td>
<td>n.a.</td>
<td>5.00</td>
<td>0.15</td>
<td>3738</td>
<td>42</td>
</tr>
<tr>
<td>S09-62c-2 MI3</td>
<td>Opx</td>
<td>C</td>
<td>70.5</td>
<td>n.a.</td>
<td>4.50</td>
<td>0.14</td>
<td>3810</td>
<td>71</td>
</tr>
<tr>
<td>S09-62i-2 MI3</td>
<td>Cpx</td>
<td>C</td>
<td>70.2</td>
<td>n.a.</td>
<td>5.55</td>
<td>0.56</td>
<td>2635</td>
<td>80</td>
</tr>
<tr>
<td>S09-62i-2 MI4</td>
<td>Cpx</td>
<td>C</td>
<td>71.1</td>
<td>39.9</td>
<td>5.94</td>
<td>0.59</td>
<td>2638</td>
<td>166</td>
</tr>
</tbody>
</table>

*SiO2 used by default for water content calculation
n.a.: not analysed
Table 4. Volatile compositions of the melt inclusions (MI) from SIMS measurements. 4a. Minoan melt inclusions, 4b. Cape Riva, 4c. Lower Pumice 2, 4d. Lower Pumice 1.

Plg: plagioclase; Opx: orthopyroxene; Cpx: clinopyroxene. C: crystal core; C border: the border of the core; R: crystal rim; GR: overgrowth rim; RS: resorption surface; Interm: between core and rim. An/Wo%: anorthite and wollastonite content in plagioclase and pyroxenes, respectively. H$_2$O, Cl, F and S values are the results of one or two analyses per MI, depending on the MI size. The ± symbol next to each H$_2$O, Cl, F and S values corresponds to the error taking into account the statistic error on the measurement and the error on the calibration.

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O (wt%)</td>
<td>CO$_2$ (ppm)</td>
</tr>
<tr>
<td>Minoan</td>
<td></td>
</tr>
<tr>
<td>4.55*</td>
<td>0</td>
</tr>
<tr>
<td>5.82**</td>
<td>0</td>
</tr>
<tr>
<td>Cape Riva</td>
<td></td>
</tr>
<tr>
<td>4.96*</td>
<td>0</td>
</tr>
<tr>
<td>6.61**</td>
<td>0</td>
</tr>
<tr>
<td>LP2</td>
<td></td>
</tr>
<tr>
<td>3.94*</td>
<td>0</td>
</tr>
<tr>
<td>5.34**</td>
<td>0</td>
</tr>
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<tr>
<td>4.48*</td>
<td>0</td>
</tr>
<tr>
<td>6.26**</td>
<td>0</td>
</tr>
</tbody>
</table>

* Mean H$_2$O (wt%) from plagioclase- and pyroxene-hosted melt inclusions

** Highest H$_2$O (wt%) measured in plagioclase- and pyroxene-hosted melt inclusions (Table 4)

H$_2$O$_{\text{m}}$ and OH$_{\text{m}}$: molecular H$_2$O and OH

Table 5. H$_2$O-saturation pressure estimates for rhyolitic melts made with VolatileCalc

Table 5. H$_2$O-saturation pressure estimates for rhyolitic melts made using the VolatileCalc software (Newman & Lowenstern, 2002).

ELECTRONIC APPENDICES
Electronic Appendix 1. Experimental phase compositions of the Minoan rhyodacite, 1a. Anhydrous compositions of the experimental glasses (wt%), 1b. Experimental plagioclase, 1c. orthopyroxene, 1d. clinopyroxene, 1e. amphibole, 1f. Fe-Ti oxides.

Electronic Appendix 2. Experimental phase compositions of the Cape Riva dacite, 2a. Anhydrous compositions of the experimental glasses (wt%), 2b. Experimental plagioclase, 2c. orthopyroxene, 2d. clinopyroxene, 2e. amphibole, 2f. Fe-Ti oxides.

Electronic Appendix 3. Experimental phase compositions of the LP2 rhyodacite, 3a. Anhydrous compositions of the experimental glasses (wt%), 3b. Experimental plagioclase, 3c. orthopyroxene, 3d. amphibole, 3e. Fe-Ti oxides.

Electronic Appendix 4. Experimental phase compositions of the LP1 rhyodacite, 4a. Anhydrous compositions of the experimental glasses (wt%), 4b. Experimental plagioclase, 4c. orthopyroxene, 4d. clinopyroxene, 4e. Fe-Ti oxides.


Electronic Appendix 6. Phase proportions (wt%) and crystallinities (wt%) of the natural samples, determined by mass balance calculations.